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THE CHEMICAL ACTION of ULTRAVIOLET RAYS

by
CARLETON ELLIS
and
ALFRED A. WELLS

Revised and Enlarged Edition
by
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of mercury discharge tubes. The Atlas Electric Devices Co. and the National Carbon Co have furnished numerous illustrations. Many authors and publishers of books and journals, too numerous to mention, have permitted the publication of illustrations from their work. Drs. D. A. Wells, W. M. Burgess and the late Albert Sherman have read certain chapters and offered valuable suggestions. The authors of the first edition have been especially helpful. Many reference books, review articles and incidental summaries, as well as abstracts of patents and other material in difficultly accessible sources, have been freely used. The effort has been made to acknowledge these in suitable places.

FRANCIS F. HEYROTH.

Institute of Scientific Research
University of Cincinnati
June, 1940

Contents

	PAGE
PREFACE	iii
CHAPTER 1. INTRODUCTION: NATURE OF ULTRAVIOLET RADIATION.....	1
Magnitude of Solar Energy—Nature of Radiant Energy Wave-length and Its Measurement—1 Fundamental Concepts and Methods 2. Units—Invisible Radiations—Radiations Beyond the Violet—The Electromagnetic Spectrum as a Whole.	
Part I	
The Sources of Ultraviolet Radiations	
CHAPTER 2. THE MECHANISM OF THE EMISSION OF RADIANT ENERGY....	15
Quantum Theory Continuous and Line Spectra—Classification of Lines and Atomic Spectra into Series Theory of the Emission of Line Spectra—The Hydrogen Spectrum Elements Other than Hydrogen The Production of Ions in Ultraviolet sources—Energy-Level Diagrams.	
CHAPTER 3. SURVEY OF SOURCES.....	30
Spark, Arc and Glow Discharges—Spark and Arc Lines Other Sources of Lesser Importance Incandescent Solids—Flames—Electrodeless Discharge.	
CHAPTER 4 THE SPARK AS A SOURCE OF ULTRAVIOLET RADIATIONS.....	38
Description Electrical Circuits for the Production of Sparks—"Hot Sparks" Arrangement of Electrodes Photochemical Reactions Produced by Sparks.	
CHAPTER 5. THE OPEN ARC.....	46
Electrical Characteristics Spectrographic Arcs Ultraviolet Sources for Photochemical Processes The Carbon Arc.	
CHAPTER 6. ENCLOSED VAPOR ARCS. THE QUARTZ MERCURY VAPOR ARC	65
Introduction Early History—Use as a Polariscopic Source—Simple Arcs Developed in the Laboratory for Photochemical Studies Development of the Commercial Quartz Mercury Arc—Nature of the Electrodes Lamps with Non mercury Anodes Sealed in Leads—Methods of Starting the Discharge—Electrical Starting Devices—The Pressure of the Mercury Vapor Commercial Mercury Vapor Arcs (Mercury Cathode Type)—Theory of Operation of the Mercury Arc. Electrical Conduction Processes at the Electrodes Conduction Processes in the Plasma, Pressure in the Arc, Operating Characteristics, Mechanism of the Emission of Radiation Continuous and Band Spectra in the Mercury Arc.	
CHAPTER 7. OUTPUT OF THE MERCURY VAPOR LAMP UNDER VARIOUS OPERATING CONDITIONS	96
Methods of Measuring Intensity of Radiations Physical Methods Chemical Actinometers—Intensities of Lines as Related to their Origins Data on the Output and Spectral Distribution of Quartz Mercury Arcs Means of Increasing the Output of the Resonance Line—The Constructed Arc—Water Cooled Arcs—Deterioration	
CHAPTER 8. RECENT MERCURY DISCHARGE LAMPS.....	131
Oxide-Coated Cathodes Lamps Employing Such Cathodes—Maiden Glow Lamps "Dual Purpose" Sources Metallic Vapor Arcs Other than the Mercury Type Manufacture of Clear Fused Quartz.	
CHAPTER 9. SOURCES OF CONTINUOUS ULTRAVIOLET RADIATIONS FOR ABSORPTION STUDIES	152
Underwater Sparks Incandescent Sources Hydrogen Discharge Tubes Theory of the Continuous Spectra of Hydrogen	

CHAPTER 10. PROTECTIVE GLASSES, ULTRAVIOLET-TRANSMITTING GLASSES AND FILTERS

Protective Glasses—Glasses Permeable to Ultraviolet Radiations—Other Ultraviolet-Transmitting Materials—Data on the Transmission of Various Ultraviolet-Permeable Materials—Durability of Ultraviolet-Transmitting Materials—Filters—Filters for "Black Light"—Filters Excluding Various Ultraviolet Regions—Transmission by Textiles—Physical Methods for Isolating Lines or Wave-length Bands—Christiansen Filters—Focal Separation—Monochromators.

CHAPTER 11. THE SUN AS A SOURCE OF ULTRAVIOLET RADIATIONS.....

The Sun's Output of Radiant Energy—Effects of the Earth's Atmosphere—Limits of the Solar Spectrum—Amounts and Distribution of the Solar Ultraviolet.

Part II

Photochemical Processes

CHAPTER 12. INTRODUCTION TO THE MECHANISM OF PHOTOCHEMICAL PROCESSES

Historical Development—The Einstein Photochemical Equivalence Law—Reactions Produced by X-Rays—The Infrared Region—The Applicability of the Einstein Law—Chain Reactions—The Nature of the Primary Process.

CHAPTER 13. MOLECULAR SPECTRA IN RELATION TO PHOTOCHEMISTRY...

Nature and Origin of Molecular Spectra—Pure Rotation Bands and the Information They Yield—Vibration-Rotation Bands—Raman Spectra—Electronic Band Spectra—Isotopes in Band Spectra—Bibliography

CHAPTER 14. SPECTROSCOPIC EVIDENCE FOR DISSOCIATION AS THE PRIMARY PHOTOCHEMICAL PROCESS

Introduction—Interpretations of Continuous Regions in Spectra—Potential Energy Curves—Excited Atoms Formed by Dissociation—Homopolar and Heteropolar Molecules—Predissociation Spectra.

CHAPTER 15. OVERALL PHOTOCHEMICAL REACTIONS

Introduction—Photochemical Thresholds—Temperature Coefficients—Kinetics of Photochemical Reactions—Effects of Intermittent and Polychromatic Light

CHAPTER 16. PHOTOSENSITIZED PROCESSES.....

Effects of Excited Mercury Atoms—Mercury Sensitized Reactions—Other Types of Photosensitization—Photochemical Reactions in Surfaces—Chemoluminescence—Photochemistry and Optical Activity—Phototropy—Related Physical Phenomena—Photophoresis—Photoelectric Phenomena.

CHAPTER 17. REACTIONS OF INORGANIC GASES THE HYDROGEN HALIDES

Measurement of Ultraviolet Absorption Spectra—Formation and Decomposition of the Hydrogen Halides—Decomposition of Hydrogen Iodide—Absorption of Hydrogen, Iodine and Hydrogen Iodide—The Other Hydrogen Halides—Absorption of Bromine—Absorption by Hydrogen Bromide—Combination of Hydrogen and Bromine—Interhalogen Compounds.

CHAPTER 18. THE HYDROGEN-CHLORINE COMBINATION.....

Spectral Absorption Data—Budden Effect—Present Viewpoint—Historical Discussion—Induction Period—Effects of Water Vapor—Chain Mechanisms—Kinetics—Thresholds and Effects of Various Wave-lengths.

CHAPTER 19. REACTIONS OF INORGANIC GASES OTHER THAN HALOGEN HYDRIDES

Spectroscopy of Oxygen—Formation and Decomposition of Ozone—Chlorine-Sensitized Decomposition of Ozone—Formation and Decomposition of Water—Hydrogen Peroxide—The Mercury-Sensitized Reaction—Decomposition of Hydrogen Peroxide—Oxidation of Hydrogen Iodide—Reactions of Oxides of Chlorine—Chlorine Monoxide—Chlorine Dioxide—Reactions of Carbon Compounds—Photolysis of Carbon Dioxide—Carbon Monoxide—Formation of Phosgene—Decomposition of Phosgene—Nitrogen Compounds—Ammonia—Decomposition of Hydrazine—Decomposition of Hydrogen Azide—Oxides of Nitrogen—Nitrous Oxide—Nitric Oxide—Nitrogen Peroxide—Nitrogen Pentoxide—Nitrosyl Chloride—Nitrogen Trichloride—Sulfur Compounds—Oxides of Sulfur—Oxidation of Sulfur Dioxide—Sulfuryl Chloride—Phosphine and Arsine—Other Elements.

	PAGE
CHAPTER 20. INORGANIC REACTIONS IN LIQUIDS.	335
General Characteristics Absorption Spectra—"Electron-Affinity" Spectra—Water and Hydrogen Peroxide—Halogens and Alkyl Halides—Oxidation of Iodides—Bromine—Chlorine—Chlorine Monoxide—Chlorine Dioxide—Chlorates—Fluorine Oxide—Nitrogen Compounds—Ammonia Nitrites Nitrates Other Nitrogen Compounds—Compounds of Sulfur—Hydrogen Sulfide—Sulphates—Persulfates—Ammonium Thiocyanate—Arsenic and Antimony Compounds—Metals and Salts—Iron Salts—Ferrocyanides and Other Complex Salts—Manganese and Chromium—Tin Compounds—Mercury and Its Compounds—Cobalt and Nickel—Tungsten and Molybdenum—The Rare Earths—Uranium Compounds—Zinc Oxide as sensitizer.	
CHAPTER 21. PHOTOCHEMICAL REACTIONS OF INORGANIC SOLIDS.	372
Alkali Halides—Silver Halides and the Latent Photographic Image—Herschel Effect—Photographic Sensitization—Ultraviolet Plates—Russell Effect—Weigert Effect—Other Silver Compounds The Blackening of Lithopones Effects of Ultraviolet Radiations on Colloidal Systems Preparation of Colloidal Systems as Affected by Radiations—Effects on the Stability of Colloidal Systems—Stratification as Affected by Light	
CHAPTER 22. REACTIONS OF ORGANIC COMPOUNDS. SATURATED ALIPHATIC HYDROCARBONS, ALKYL HALIDES AND ALCOHOLS.	393
Introduction—Saturated Hydrocarbons—Alkyl Halides—Absorption Data—Reactions of Alkyl Halides Alcohols Glycerol Ethers	
CHAPTER 23. REACTIONS OF UNSATURATED ALIPHATIC COMPOUNDS, ALDEHYDES AND KETONES AND CARBOHYDRATES.	406
General Behavior of Unsaturated Compounds Simple Decompositions Polymerizations—Stereoisomeric Transformations—Other Types of Isomerization Acetylene Aldehydes and Ketones Absorption by Aldehydes and Ketones Reactions of Aldehydes—Acetaldehyde Oxidation of Aldehydes Unsaturated Aldehydes Ketones—Acetone—Ketone—Diketones The Carbohydrates Monosaccharides Disaccharides—Polysaccharides	
CHAPTER 24. REACTIONS OF ACIDS AND OTHER ALIPHATIC COMPOUNDS.	437
Introduction Photolysis of Formic Acid Dibasic Acids Complex Oxalate Ions—The Eder Reaction—Action of Iodine on Potassium Oxalate—Malonic and Other Acids—Hydroxylic Acids—Lactic Acid—Tartaric Acid Keto Acids—Halogenated Acids—Unsaturated Acids The Malic Fumaric Transformation—Compounds Containing Nitrogen—Cyanogen and Its Compounds Amines Amides—Azomethane Diazo Compounds—Nitro-Compounds Sulfur Compounds Organometallic Compounds	
CHAPTER 25. REACTIONS OF AROMATIC COMPOUNDS.	466
Hydrocarbons—Anthraquinone Sensitized Oxidation of Toluene Substitution Products of Benzene—Photochemical Nitritations Nitro Compounds—Benzaldehyde and Its Oxidation—Transformations of <i>o</i> -Nitro benzaldehyde to Nitrosobenzene Acid Aromatic Ketones—Phenols—Quinones—Aromatic Acids and Their Derivatives Benzoic Acid—Salicylic Acid Mandelic Acid Phthalates Cinnamic Aldehyde and Cinnamic Acids Halogenation of Cinnamic Acid Coumarin and Its Derivatives Other Aromatic Compounds with Unsaturated Side Chains—Styrenes Chalcone—Benzal Pyruvates and Benzoyl Acrylates Other Compounds Phototropy Stereoisomerism of Oximes and Semicarbazones—Aromatic Amines Aniline and Related Compounds Migrations in <i>N</i> -Substituted Amines—Condensation Reactions of Amines Color Reactions of Amines Azo, Diazo and Related Compounds Other Compounds	
CHAPTER 26. REACTIONS OF COMPOUNDS WITH CONDENSED RING SYSTEMS.	501
Naphthalene Derivatives Naphthoquinone Anthracene and Its Polymerization—Various Anthracene Derivatives Anthraquinones and Their Use in Photochemical Oxidations—Oxidation of Anthracene Naphthalenes Rubrene Other Hydrocarbons	
CHAPTER 27. REACTIONS OF COMPOUNDS WITH HETEROCYCLIC RINGS.	513
Essential Oils and Their Constituents Other Compounds with Oxygen in the Ring—Compounds with Nitrogen in the Ring Hydantoins Pyrimidines Pyrrole—Picoline Pyridine and "Photopyridine" Alkaloids Nicotine Quinine and Its Oxidation by Chromic Acid—Other Alkaloids	
CHAPTER 28. EFFECTS OF LIGHT ON HALOGENATION REACTIONS.	526
Introduction Aliphatic Hydrocarbons—Chlorination of Natural Gas—Chlorination of Chloroform—Unsaturated Hydrocarbons Action of Iodine on Unsaturated Hydrocarbons—Other Aliphatic Compounds—Acids and Their Salts—Cyclic Compounds Aromatic Compounds—Halogenation of Benzene and Its Halides—Chlorination of Toluene—Other Aromatic Compounds—Naphthalene, Anthracene and Related Compounds Terpenes—Other Substances	

Part III

Applications of Photochemistry to Industrial Products

CHAPTER 29. THE REACTIONS OF FATTY ACIDS AND THE PRESERVATION OF FOODS	553
Oxidation of Fatty Acids—Other Reactions of Fatty Acids—Absorption and Fluorescence of Oils—Photochemical Changes of Various Oils, Chiefly Edible Oils—Oxidation of Oils—Rancidity in Fats—Effects of Colors of Protective Wrappers in Preserving Foods from the Development of Rancidity.	
CHAPTER 30. PROCESSES INVOLVING THE POLYMERIZATION OF OILS. PAINTS AND VARNISHES	564
Changes in Tung Oil—Photochemical Behavior of Linseed Oil—Drying of Oils—Effects of Light on Pigments—Accelerated Weathering Tests for Paints—Light Sources for Testing Apparatus—Proposed Exposure Cycles—Reflection and Absorption of Light by Paints—Artificial Resins—Varnishes and Lacquers—Accelerated Tests for Varnishes—Nitro-Cellulose Lacquers—Protective Overcoatings.	
CHAPTER 31. PHOTOCHEMISTRY OF RUBBER.....	593
Polymerizations and Depolymerizations—Vulcanization by Ultraviolet Rays—Fluorescence Tests for Accelerators—Light and the Oxidation of Rubber—Accelerated Weathering Tests—Protection of Rubber from the Destructive Action of Light—Bonding Rubber to Other Materials—Chlorinated Rubber.	
CHAPTER 32. TEXTILES, PAPER AND DYESTUFFS.....	613
Deterioration of Textiles by Light—Cotton and Cellulose—Deterioration Aided by Certain Dyestuffs—Paper and Wood Pulp—Fluorescence Tests for Paper Products—Artificial Silk—Silk—Wool—Photochemistry of Dyes—Diazo-Compounds—Azo Dyes—Triphenylmethyl—Triphenylmethane Dyes—Use of Malachite Green—Leuco Cyanide in Actinometry—Phthalein Dyes—Methylene Blue—Other Dyestuffs—Bleaching of Dyes—Tests for the Light Fastness of Dyes—Sunlight Tests—Use of Artificial Sources—Behavior of Various Types of Dyestuffs—Inks—Fluorescence Tests for Dyes—Textile Printing—Diazo Photographic Papers—Miscellaneous Processes.	
CHAPTER 33. MISCELLANEOUS APPLICATIONS OF ULTRAVIOLET LIGHT... ..	650
Patent Leather—Leather Products—Fluorescence Tests for Leather—Petroleum Products—Absorption of Light by Petroleum Products—Light Stability of Petroleum Distillates—Color Changes and Gum Formation—Use of Ultraviolet Light in Testing Gasolines—Other Applications to Petroleum Products—Drugs and Related Products—Tobacco—Alcoholic Beverages—Miscellaneous Products—Asphalt—Fertilizers—Linoleum—Spectrographic Analysis—Fluorescence Analysis	

Part IV

Applications of Ultraviolet Rays in Biology

CHAPTER 34. PHOTOCHEMICAL BEHAVIOR OF COMPOUNDS OF BIOLOGICAL SIGNIFICANCE	669
Lipins—Amino-Acids—Tryptophane, Tyrosine, etc.—Behavior of Proteins—Enzymes—Diastase—Sucrase—Lipase—Proteinases—Enzymes Concerned with Respiration—Hormones—Products of Pathological Significance—Tuberculin—Toxins.	
CHAPTER 35. THE LETHAL ACTION OF ULTRAVIOLET RAYS AND STERILIZATION	692
Early History—Bactericidal Spectral Regions According to Earlier Observers—Interpretations of the Lethal Mechanism—Role of Nucleic Acids—Number of Quanta Required per Bacterium—Action of Ultraviolet Rays on Yeasts—The Question of the Stimulation of Yeast Growth—Fermentation—Molds—Viruses and Bacteriophages—Algae—Higher Plants—Protozoa—Eggs, Embryos, Lower Animal Forms—Applications—Sterilization of Water—Sterilization of Milk and Other Opaque Substances—Food Products—Vaccines—Pharmaceutical Products—Various Products—Action of Irradiated Oils—Sterilization of Air.	

	PAGE
CHAPTER 36. THE PHYSIOLOGICAL EFFECTS OF ULTRAVIOLET RAYS.....	732
Introduction Effects on the Skin—Absorption by the Skin Erythema and Pigmentation—Sunburn Creams and Protective Salves—Effects of Light on Metabolism and the Circulation Effects on the Blood—Hemolysis—Blood Sugar and Carbohydrate Metabolism—The Blood pH—Blood Enzymes—Effects on Immune Bodies in the Blood—Growth—Effects on the Secretory Activity of Glands—Production of Milk—Effects of Ultraviolet Light on the Eye Media—Effects on the Development of Simple Organisms—Relation of Ultraviolet Light to Neoplasms Miscellaneous Effects on Various Organisms—Mitogenetic Radiations	
CHAPTER 37. THERAPEUTIC APPLICATIONS OF ULTRAVIOLET LIGHT EXCLUSIVE OF RICKETS	769
Local Therapy—Applications in Dermatology—General Body Irradiation—Heliotherapy—Methods of Application of Artificial Sources—Suggested Mechanisms—Effects on Resistance to Disease—Limitations	
CHAPTER 38. RICKETS AND IRRADIATION	778
Rickets—History of Introduction of Ultraviolet Therapy Effective Wave-Length Regions—Amounts of Energy Required and Amounts Available from the Sun at Various Seasons and Locations Effects on Mineral Metabolism—Applications in Animal Husbandry—Irradiation and Poultry Culture—Irradiation of Foodstuffs	
CHAPTER 39 THE PHOTOCHEMISTRY OF THE FORMATION OF VITAMIN D..	791
Early Observations Regarding the Precursor Early Views as to the Change Involved Ultraviolet Absorption Studies Indicate Ergosterol to be a Provitamin—Information Yielded by Studies of the Changes in Ultraviolet Absorption by Ergosterol During Irradiation Quantum Yields Other Features of the Irradiation Changes—Isolation of Crystallized Irradiation Products Chemical Changes Occurring During the Irradiation of Ergosterol Other Antirachitic Compounds Products Related to Cholesterol as Precursors of the Natural Vitamin Color Tests and Assays—Physiological Effects—Dosage and Standardization Toxic Effects Hypervitaminosis D—Relation to Tuberculosis—Other Effects	
CHAPTER 40 COMMERCIAL PRODUCTION OF VITAMIN D	827
History Patent Proposals for the Irradiation of Foods Pharmaceutical Developments—Methods for Increasing Vitamin D in Milk—Commercial Irradiation of Milk—Soaps and Skin Creams and Vitamin D	
CHAPTER 41 ULTRAVIOLET LIGHT AND OTHER VITAMINS	848
Vitamin C Vitamins of the B Group Irradiation Used in the Determination of the Constitution of the Flavins—Absorption of Ultraviolet Light by Vitamin A—Destruction of Vitamin A by Irradiation Other Vitamins—Photochemistry of Vision	
CHAPTER 42. PHOTOSENSITIZED BIOLOGICAL PROCESSES	860
Photodynamic Action Effects of Hematoporphyrin—Theories of the Sensitization Mechanism	
CHAPTER 43 PHOTOSYNTHESIS OF CARBOHYDRATES.....	866
Introduction Formaldehyde as Intermediate Attempts to Obtain Photosynthesis Without Chlorophyll—Work of Baly The Physiological Mechanism—Action of Light on Chlorophyll—Relation of Chlorophyll to Photosynthesis—Mode of Action of Chlorophyll—Quantum Yields—Blackman Reaction—Various Interpretations of the Mechanism—Photosynthetic Units Photosynthesis of Proteins	
CHAPTER 44. EFFECTS OF ULTRAVIOLET RADIATIONS ON PLANTS.....	885
The Question of Stimulation—Observations of Papp on Germination and Growth of Seedlings—Effects on More Mature Plants—Effects on Formation and Destruction of Chlorophyll and Other Plant Pigments—Miscellaneous Effects	
AUTHOR INDEX	893
SUBJECT INDEX	923

Chapter 1

Introduction: Nature of Ultraviolet Radiation

The agency of light and the field of photochemistry, aside from photography, have until recently received relatively little use on a commercial scale. To be sure, a few photochemical processes of an industrial character, such as the production of benzyl chloride, have had a limited commercial application, but most chemical operations utilizing the agency of sunlight have been found slow and ineffective. In contrast with the industrial applications, theoretical photochemistry has recently attracted many workers, and a few guiding principles, together with a considerable amount of detailed information, have been obtained during the past three decades. Much of this advance has been due to the study of the effects of ultraviolet radiation which, following the development of suitable sources, has been carried on with vigor.

Everyone is familiar with the application of ultraviolet irradiation methods to the problem of enriching the vitamin D content of milk and of certain other food-stuffs and pharmaceutical products. The number of branches of chemistry in which this radiation has been studied is, however, often a source of surprise to chemists when they first become cognizant of the facts. This is largely because comparatively few industrial operations are carried out with this form of radiant energy.

Foodstuffs, the fuels which supply the energy of all animal life, are built up by the action of sunlight in plants. Desirable as it might be to develop ways of replacing the present farming methods by well-controlled photochemical operations conducted in a factory, this is of less immediate importance than the problem of the exhaustion of natural fuels which serve as sources of energy for our mechanized civilization. Coal and oil represent the stored vegetation of the past. In an address on the future problems of engineering, Parsons¹ pointed out the limitations imposed by thermodynamics upon the utilization of fuels and emphasized the imminent need for studies of the availability of other sources of energy. After considering hydro-electric power sources and the other less explored possible sources of energy such as the atom, the heat of the earth, tides, waves and wind, he concluded that the most promising source is the sun. For the utilization of solar energy it may be necessary to find reactions which will yield compounds of high energy content which can serve as storage reservoirs.

MAGNITUDE OF SOLAR ENERGY

From the time of Joseph Henry, workers at the Smithsonian Institution, including particularly S. P. Langley and, at present, Charles Abbot, have made many measurements of the total amount of energy received on the earth from the sun at a number of stations throughout the world. The solar constant is defined as the solar energy which impinges in unit time on unit area of a surface perpendicular to a sunbeam just outside the earth's atmosphere. Observations made at the

¹ Parsons, W. B., *J. Frank. Inst.*, **200**, 219 (1925).

earth's surface are corrected for the loss of about 30 per cent which occurs during the passage of the light through the atmosphere. The mean value of the solar constant has been found to be 1.94 calories per minute per square centimeter, equivalent to 1.35×10^6 ergs per square centimeter per second. The fluctuations of 2 to 3 per cent on both sides of the mean appear to be associated with the eleven-year sunspot cycles, the radiation being greatest when the spots are most numerous.

Stewart² has made calculations which enable one to visualize the meaning of these figures in comparison with the amounts of energy available from other sources. He concludes that the sun at the zenith supplies the outer atmosphere with 4,690,000 horsepower per square mile. At the surface this is equivalent to about $4,690,000 \cos \theta \times (0.70)^{\sec \theta}$ where θ is the angle between the sun and the zenith. The maximum power output of Niagara Falls is estimated at about 4,000,000 H.P. At noon on a clear day in June, the sunlight falling on 133 square miles at Philadelphia is equivalent in power to 100 Niagaras; it is about 70 per cent less in December. If the radiation which strikes the whole earth in a single second could be converted into power, its value, at one cent per kilowatt-hour, would be nearly half a billion dollars. Parsons stated that, assuming the total span of daily sunlight to be equal to nine hours of maximum intensity and 50 per cent of the energy to be recoverable, a strip of land 10 miles wide and 100 miles long would develop daily as much power as could have been obtained from one-half the world's total fuel consumption in 1920, allowing three pounds of coal per horsepower. The area of Salt Lake, Utah, alone would suffice to produce energy equal to that furnished by the whole annual world consumption of coal.

As the earth intercepts only one part in 22,000 millions of the total energy radiated by the sun, it may be calculated that the sun emits nearly 75,000 H.P. per square yard of its surface. At one cent per kilowatt-hour, its power output would be valued at "a billion dollars in a billionth of a second."

Attempts made thus far to utilize this energy have been limited to the use of aqueous vapor as an intermediary in an engine operated by very low steam pressure. According to Parsons, the maximum overall efficiency obtained in the Shuman-Boys absorber in Meadi, Egypt, was 4.32 per cent. As yet few, if any, attempts have been made to concentrate the sun's rays by a system of reflectors upon chemicals in order to get the latter to react to produce others of high energy content and fuel value.

The conscious development of such ideas has instead been concentrated largely upon the problem of the mechanism by which chlorophyll enables plants to utilize solar energy in building up the compounds which serve as foods.

NATURE OF RADIANT ENERGY

An understanding of the chemical reactions produced by ultraviolet radiations requires a knowledge of their physical nature. As they represent but one of the forms of radiant energy which comprise what is called the electromagnetic spectrum, there is given in the following portions of this chapter a brief historical sketch of the present knowledge of light, visible and invisible. There is an essential physical unity in the nature of wireless waves, infrared radiation, visible light, ultraviolet radiation, x-rays and gamma-rays. Photochemical changes induced by visible light and by ultraviolet radiations are quite similar in mechanism, differing chiefly in the amounts of energy involved and in the types of equipment necessary.

² Stewart, J. Q., *J. Frank. Inst.*, 204, 438 (1927).

These two forms of radiant energy are distinguished by special names merely because our eyes permit us to appreciate the presence of the visible but not of the ultraviolet radiations.

Since 1913 conceptions derived from the study of the mechanism of the production, transmission and absorption of radiations have come to dominate and transform modern chemistry and physics. They have been applied with great success to the problem of the constitution of the atom, affording models by which to express the facts embodied in the periodic table. Very recently, they have led to new methods of studying the nature and strength of the chemical bond and have given rise to a new attack on the fundamental problem of chemical affinity.

Each of the forms of radiant energy is transmitted through a vacuum at the same rate, 186,000 miles per second or 3×10^{10} centimeters per second, the long-known velocity of light. The manner in which light is transmitted through space has been for more than two centuries the subject of a controversy between the adherents of the wave and corpuscular theories, the origin of neither of which is certain.³

The inadequacy of a corpuscular theory to account for the phenomena of diffraction and interference led Huyghens in 1690 to state, without claiming the idea as his own, that light is made up of waves which he conceived as longitudinal pulses extending in all directions from a center of disturbance along a spherical front. He did not, however, conceive of the existence of a train of waves. Newton, the discoverer of the resolution of white light into a spectrum by means of a prism, on the other hand, favored the view that light is transmitted as minute corpuscles ejected through space, since he believed (1672) that a wave theory could not account for the rectilinear propagation of light. He described the phenomena of diffraction of light passing between closely spaced knife edges and the famous rings of color observed in thin plates, now known to be due to interference. Both of these phenomena now, as then, afford the strongest evidence for the wave nature of light. Newton⁴ ascribed them to certain "fits" of reflection or transmission. Notwithstanding the fact that Huyghens had shown it possible to explain the rectilinear propagation of light and the phenomena of refraction by certain geometrical constructions regarding the advancing wave form, confusion reigned for about a century.

By extending the wave theory to include a continuous series of periodic waves, Dr. Thomas Young was able to explain the phenomenon of interference and to demonstrate it in a famous experiment in a Bakerian Lecture before the Royal Society in 1801. Light from a single source was made to pass through two very closely adjacent pinholes and illuminate a spot upon a screen. At the spot where the two cones of light overlapped, dark and light bands are observed. Any point within this area receives light by two different paths, one from each pinhole. If the lengths of these paths differ, the crest of a wave reaching it by one path may meet the trough of a wave reaching it by the other; with a different ratio of the lengths of the paths, a spot nearby may receive the crests of both waves. In the former case the crest and trough (then believed to be points of maximum compression and rarefaction) annul each other, are said to interfere, and the spot receives no illumination. In the latter case the waves add together and the spot is very bright.

This experiment regarding the nature of interference turned the tide in favor of the wave theory of light. In the early theory, the waves were conceived as

³ Crew, H., *J. Opt. Soc. Am.*, 20, 6 (1930).

⁴ Newton, Sir Isaac, "Optics," 1704.

longitudinal compressions and rarefactions of the ether similar to those by which sound is transmitted by air. New difficulties were introduced by the discovery of the phenomenon of the polarization of light (Malus, 1809) and the investigation by Arago of the rotation of the plane of polarization by various substances. These phenomena, unlike any encountered in the case of sound, eluded explanation until Fresnel in 1821 published the brilliant suggestion that the light waves may be vibrations transverse to the direction of propagation of the spherical wave-front.

WAVE-LENGTH AND ITS MEASUREMENT

1. *Fundamental Concepts and Methods.* The distance from crest to crest or trough to trough of a series of waves is known as the wave-length. For visible light it is very small and must be measured in suitable small units. That the wave-length has for each color a constant and characteristic value was indicated by later interference experiments of Young.

While all colors of light travel at the same rate in a vacuum, this is not the case when they pass through transparent material bodies. In going from a light medium to a denser one the velocity of light is slowed to an extent which depends upon the wave-length. For this reason, white light in passing through a prism is spread out into a spectrum of colors. The greater the thickness of the path of light in the prism the greater the resolution or spreading of the spectral colors. Measurements of the wave-length of light in some limited spectral regions, as for example the yellow, were early made by means of an experimental arrangement based upon the interference of waves reaching a spot along paths of slightly different lengths.

For precise measurements of this sort the particular region at which the measurement is made must be reproducibly defined. Fraunhofer found in the solar spectrum a series of dark lines which serve as natural landmarks for certain wave-lengths, rendering the location of a given point in the spectrum possible irrespective of the resolution of the prism. It was later found that these lines correspond in wave-length to the bright lines found to be superposed on a continuous colored background when certain elements are heated to high temperatures. Kirchhoff found that the elements which emit these lines are also capable of absorbing them when the vapors of the elements are placed between a continuous source and the spectrograph. The theory of the origin of the Fraunhofer lines in the solar spectrum is that certain elements in the gaseous atmosphere of the sun absorb the sun's radiations at just these wave-lengths, and so lessen their brilliance in the solar spectrum.

In 1823 Fraunhofer made precise measurements of the wave-lengths of the chief dark lines which occur in the solar spectrum. He employed for this an instrument based upon the principle of interference, the optical grating. With a diamond, he ruled a great number of equally and very closely spaced parallel lines in a thin film of gold deposited on a glass plate. This grating simulates a prism in its ability to separate the wave-lengths of light; unlike the prism it permits the wave-length of any line to be measured by direct methods described in detail in any textbook on optics.

Because of the likelihood of mechanical imperfections in the ruling of even the best gratings (such as those ruled by Rowland) Michelson, in 1893, turned to the use of interferential apparatus. This represents a simplification of the principle of the diffraction grating, since the many thousands of waves which act simultaneously in grating experiments are, in the interferometer, replaced by but two with a very large difference in path. The interferometer offers resolution prac-

tically without limit. Its use showed that spectral lines are often accompanied by other lines called "satellites" and made possible the development of modern theories of the multiplicity of spectral lines.

With the help of Benoit in the Bureau Internationale des Poids et Mesures, Michelson determined the wave-length of the cadmium red line with a precision far beyond that of all previous workers. By the use of a new interferometer, Fabry in 1900 and Perot⁵ compared the wave-length of the red cadmium line with the standard meter in Paris and found the wave-length to be equal to 0.00064384696 mm., the observations being taken in dry air at 18°C. and at a mercury pressure of 76 cm. This value agreed well with that of Michelson who reported 0.00064384700 mm. for the same line. Seven years later Fabry and Buisson investigated certain other wave-lengths and from these measurements there developed the international system of wave-lengths, the precision of which is probably one part in a million in absolute as well as in relative values. Standard values for many lines can be found in the "International Tables of Critical Constants." It may at first seem that such precision is unnecessary. Recently, however, numerical relations have been discovered between the wave-lengths of different spectral lines emitted by the same element and these have led to the development of theories of atomic structure. At the present time the details of the structures of individual lines are being actively investigated. This work requires data of high precision.

2. *Units.* The minuteness of the wave-lengths of the colors of visible light makes it desirable to express them in terms of units of length much smaller than the millimeter. In the ultraviolet, and sometimes also in the visible range, the Ångström unit is employed. This is defined as 1×10^{-8} cm. It is commonly abbreviated by the letter A rather than the Swedish Å. The cadmium red line is 6438.4696 Å. In the visible region many workers employ a unit, ten times as large as the Ångström (10 Å), called the millimicron. A micron is the millionth part of a meter and the millimicron is the thousandth part of this, since *milli* in the metric system means "the thousandth part of" the unit to which the term is prefixed. It is correctly designated by the symbol $m\mu$, since the letter "m" is the standard abbreviation for milli, and μ that for the micron or, in general, "millionth part of."⁶

Another manner of designating or identifying a given radiation is based upon the velocity with which light travels in a vacuum. The number of wave crests which pass a given point in a second, *i.e.*, the frequency of the light, is obtained by dividing the velocity of light expressed in centimeters per second by the wave-length in question expressed in centimeters. Frequencies are of importance in connection with modern views of the mechanism of the emission of light from hot bodies. They involve very large and unwieldy numbers.

Smaller figures may be obtained by dividing the true frequencies by the velocity of light. The units so obtained are known as wave-numbers and represent the number of crests within a distance of one centimeter of a wave-train viewed instantaneously. The wave-number is obviously the reciprocal of the wave-length expressed in centimeters, rather than in Ångström units. It has been much employed in recording the data of spectroscopy.

⁵ This account has been derived largely from an address by Charles Fabry, The Franklin Institute Centenary Lecture, Sept. 17, 1924.

⁶ Following Kayser, the German authority on spectroscopy, the millimicron has been abbreviated as $m\mu$ by many writers. This is erroneous since it would logically mean the millionth part of the millionth part of a meter. The error was pointed out by Guillaume, director of the International Bureau of Weights and Measures in 1913, but the misleading symbol is still frequently encountered. Camp, J. P., *Science*, 70, 453 (1929); Dorsey, N. E., *Ibid.*, 71, 67 (1930).

INVISIBLE RADIATIONS

The visible spectrum covers only the short range of wave-lengths from 7200-7600A at the red end to 3900-4000A at the violet end, the exact limits varying from one person to another, and from one species of animals to another. In 1800, Sir William Herschel discovered that the heating effect of sunlight was not confined to the visible portion of the spectrum from a prism since a thermometer placed beyond the red end where nothing could be seen showed a higher temperature than when exposed to the red rays. About this time the existence of some form of energy beyond the violet end of the spectrum was demonstrated independently by Ritter and by Wollaston (1802). They showed that the decomposition of silver chloride (which occurs in the visible range as shown by Scheele in 1777) proceeded even more rapidly in the invisible region.

It was soon noted that both the heating effects of the infrared region and the chemical activity of the ultraviolet region are due to radiations of the same general nature as those producing visible light. Thomas Young showed the energy in the ultraviolet to be of wave nature by obtaining records on silver chloride paper of interference rings produced in this region. Phenomena of diffraction and interference were demonstrated in the infrared by Fizeau and Foucault in 1847. The occurrence of Fraunhofer lines in the infrared region of the sun's spectrum was demonstrated by Herschel in 1840; Becquerel photographed them in the ultraviolet region.

In 1860, James Clerk Maxwell laid the foundations of the modern theory of all these radiations by relating the mathematical theories of Green, Stokes and Kelvin, for wave motion as a generalized process, to the experimental demonstrations by Faraday of the electromagnetic fields set up by the motion of electric charges. He showed on theoretical grounds that electromagnetic waves should travel with the velocity of light and indicated that all these forms of radiant energy consist of such waves.

Fitzgerald showed in 1883 that a coil carrying a rapidly alternating current should radiate waves into the surrounding space. About 1886, Hertz produced these waves by means of an oscillatory discharge across a gap. He also developed methods for detecting and measuring the wave lengths of these electromagnetic waves, which can be greatly varied, and showed that they can be reflected and refracted like light. Within a few years, Marconi employed them in wireless signaling.

Radio waves are millions or billions of times longer in wave-length than are those of visible light. The waves produced by Hertz were much shorter in wave-length than those employed in radio transmission. Recently, by a refinement of the method employed by Hertz it has been possible to obtain waves having lengths of only 0.1 to 0.2 mm.⁷ These are shorter than the longest infrared rays from the mercury-vapor lamp (0.4 mm.) or the Welsbach burner (0.6 mm.) as measured by Rubens. The wave-length regions of the Hertzian and infrared waves thus overlap and there is no fundamental distinction between these forms of radiant energy. The only reason for applying different names is to emphasize the experimental techniques employed for their production.

RADIATIONS BEYOND THE VIOLET

In studying the ultraviolet region the same methods of resolution employed in the visible, the prism or the diffraction grating, have been used. For detection

⁷Nichols, E. F., and Tear, J. D., *Proc. Nat. Acad. Sci.*, 9, 211 (1923).

of the radiant energy, a photographic plate usually serves. If one passes progressively toward the short wave-lengths, the study of the ultraviolet begins with a minimum of difficulty. But as one advances into the shorter wave-lengths the difficulties increase. At about wave-length 3400A, glass becomes so strongly absorbing that it is no longer of service and must be replaced by quartz or some similar crystalline substance. At about 2900A, the solar spectrum ends, due to absorption by ozone in the higher levels of the earth's atmosphere. By the use of artificial sources, such as the metallic arc, the short wave-lengths may be supplied in satisfactory intensity. It is comparatively easy to photograph and measure wave-lengths as short as 1850A, this limit having been reached by Cornu. From this point the difficulties increase very greatly as quartz becomes strongly absorbing and the gelatin of the photographic plates becomes so opaque that the radiation does not penetrate it and so can no longer act upon the silver salt. Finally, with still shorter waves, air itself ceases to be transparent, all radiations being absorbed in a very small thickness. Schumann, working between 1890 and 1903, overcame these difficulties by replacing the quartz by fluorite, by placing the apparatus in a vacuum and by making photographic plates with emulsions containing a minimum of gelatin.⁸ By the methods of Schumann it was possible to obtain the spectrum of hydrogen to 1200A, at which point fluorite ceases to be transparent. Schneider⁹ has suggested that lithium fluoride may be employed in place of fluorite.

Schumann did not actually measure the wave-lengths but only estimated them by means of an extrapolation of the dispersion formula for fluorite. Particularly active among more recent workers in the Schumann region have been Leon and Eugene Bloch¹⁰ who studied many lines of manganese, chromium, silver, gold and platinum sparks of wave-length between 1869 and 1330A.

For working further into the ultraviolet, the concave grating is employed as the resolving medium; as in the visible range, it has the advantage of giving directly the lengths of the waves. The grating, usually of about one meter radius, is placed¹¹ in a container maintained at a very high vacuum. As, however, the gas pressure surrounding the spark which serves as the source of light cannot be too low, matters must be so arranged that the gas surrounding and carrying the discharge is not allowed to enter into the body of the spectrograph. This is done by separating the source from the rest of the apparatus by a short and narrow slit and applying a powerful mercury diffusion pump at a point just beyond this slit. With this arrangement, Lyman succeeded in determining the lengths of the waves studied by Schumann; in addition to this, he extended the optical spectra to 510A in the case of helium.

Millikan, Bowen and collaborators, as well as Edlén¹² and others, have subsequently measured lines (emitted by hot sparks) as short as 40.28A in the case of the stripped carbon atom. The existence of much shorter radiations than these had, however, been known since the discovery of x rays by Röntgen in 1895 and of gamma-rays by Villard in 1900. X-rays have wave-lengths of the order of molecular dimensions or less. Laue, in 1912, conceived the idea that the natural strata of a crystal might serve as a diffraction grating for such short wave-lengths, since the distance between the rulings would be that separating the rows of atoms

⁸ Directions for making these plates are given by Hopfield, J. J., and Appleyard, E. T. S., *J. Opt. Soc. Am.*, **22**, 488 (1932).

⁹ Schneider, E. G., *J. Opt. Soc. Am.*, **27**, 72 (1937).

¹⁰ Bloch, L. and E., *J. Phys. Radium*, **6**, 154 (1925).

¹¹ Lyman, T., *J. Frank. Inst.*, **201**, 556 (1926), *Astrophys. J.*, **60**, 1 (1924); Wood, R. W., and Lyman, T., *Phil. Mag.*, **2**, 310 (1926).

¹² Edlén, B., *Nature*, **127**, 405 (1931).

in the crystal. On sending a bundle of x-rays through a suitable crystal the expected phenomenon of diffraction appeared. A short time later, Bragg attacked the problem by studying the reflection from a crystal face and succeeded in measuring x-ray wave-lengths.

The characteristic x-rays of the elements range from 22A for the K-absorption edge of uranium to 0.107A. The longest x-rays measured by the Bragg crystal diffraction method are 21.53A, for one of the lines of chromium.¹³ Compton¹⁴ and also Thibaut¹⁵ have shown that ruled gratings of the kind used for measuring the wave-lengths of ordinary light can be employed to demonstrate the diffraction of x-rays striking the grating at very small grazing incidence. This method has been much employed in studying the region between the x-rays and the shortest ultraviolet rays.

Recent absorption measurements in the Schumann region show that many common compounds absorb these ultraviolet rays and suffer decomposition thereby. The photochemistry of this region seems destined to provide many important observations.

The physicist has made considerable progress in exploring the region of wave-lengths somewhat longer than the usual x-rays by estimating the wave-lengths by the indirect method of resonance potentials. The usual method of x-ray generation is by the bombardment of a metal target with high-speed cathode rays. A modification permits the generation of radiations within the longer wave-length range. The substance which is to emit the rays is bombarded by a stream of thermionically-produced electrons moving at lower velocities produced by accelerating them by definite alterable electrical potential differences. The energy which the bombarding electrons can give to the atoms bombarded is thus known and may be expressed as the product of the charge of the electron and the potential gradient in volts per centimeter. The energy is in this way stated in units called electron-volts. Since the charge on the electron is constant, the energy is sometimes expressed less accurately as volts, for brevity. As the acceleration of the electrons is gradually increased by raising the potential difference between a plate and a charged grid through which the electrons pass, the energy possessed by the electrons becomes great enough to enable them, on striking atoms in the gaseous space through which they pass, to excite the atoms to emit radiation. Certain critical energies (in electron-volts) are necessary for this to occur. The critical voltages are obtained in such experiments by finding certain discontinuities in the current carried by the electron stream as the charge on the grid is progressively changed. At 4.9 volts, in the case of mercury vapor as the emitting atom, a single line with a wave-length of 2537A appears. This is called the mercury resonance line. At 6.7 volts, one with a wave-length of 1844A flashes out. The frequencies corresponding to the emitted wave-lengths are calculated by dividing the energy by a fundamental constant of nature, the quantum of action or Planck's constant, the nature of which will be discussed in the next chapter.

The method has been extended to the region of wave-lengths only slightly longer than x-rays. The emission of radiations in such experiments is made evident by a sudden increase of gaseous ionization or of photoelectric effect as the accelerating voltages are gradually raised beyond the critical values. Holweck¹⁶

¹³ Thoraeus, R., *Phil. Mag.*, **1**, 312 (1926).

¹⁴ Compton, A. H., *Proc. Nat. Acad. Sci.*, **11**, 598 (1925).

¹⁵ Thibaut, J., *Compt. rend.*, **182**, 55, 1141 (1926); **185**, 62 (1927); *J. Phys. Radium*, **8**, 13 (1927); *Nature*, **121**, 321 (1928); *Physik. Z.*, **29**, 241 (1928); *J. Opt. Soc. Am.*, **17**, 145 (1928); De Broglie, *Compt. rend.*, **190**, 93 (1930).

¹⁶ Holweck, F., *Compt. rend.*, **173**, 709 (1921); *J. Chim. Phys.*, **22**, 311 (1925).

has shown that a continuous radiation is produced when accelerating voltages between 25 volts (500A) and 280 volts (44A) are employed. He used an apparatus consisting of a sort of Coolidge x-ray tube made entirely of metal in which the cathode and anode are separated by a distance of one millimeter. The tube is operated at potentials of 25 to 1800 volts. As the rays emerge from the tube through celluloid films of a thickness of 0.00005 mm., they enter an ionization chamber. Superposed on the continuous spectrum there is a line spectrum characteristic of the element used as a target.

These radiations lack penetrating power; this is the reason why it is necessary to use the thin celluloid window. They are said to be soft x-rays. The term hardness connotes penetrating power. Soft x-rays (but not as soft as those of Holweck) have been used by Günther¹⁷ in the examination of thin layers of biological products such as leaves or the wings of insects. These rays, which because of their greater ease of absorption, are better suited than hard x-rays for the treatment of skin diseases, are produced in tubes operated at voltages low (4 to 12 kilovolts) compared with those used for more penetrating x-rays. Egress is through a window of a special glass in which sodium, calcium and silicon have been replaced by lithium, beryllium and boron.

As the wave-lengths increase from the x-ray to the ultraviolet region, the absorption of the radiations by many substances increases to a maximum beyond which there is a diminution in absorption as the better-known regions of the ultraviolet are reached. Holweck found that 0.00027 mm. of celluloid, which has a relatively low absorption in comparison with other substances in this region, transmits only 3 per cent of the radiation of wave-length 310A at which it has its maximum absorption.

The gamma-rays produced by radioactive decay, as measured by Ellis, have wave-lengths between 0.26 and 0.005A. Very penetrating radiations known as cosmic rays, discovered by Wulf and by Gockel between 1909 and 1914¹⁸ have recently been the subject of particularly extensive investigation by Kolhörster, Regener, Millikan, Compton, and many others. Although some workers consider them as electromagnetic waves of extremely high frequency, most believe them to be some type of high velocity movement of minute corpuscles. They are certainly non-homogeneous, the highest frequency band has so enormous a penetrating power that it passes through 200 feet of water or 18 feet of lead before being completely absorbed, although two or three inches of lead absorb the hardest gamma-rays.

THE ELECTROMAGNETIC SPECTRUM AS A WHOLE

The radiations from wireless telegraph waves to gamma-rays which make up the electromagnetic spectrum are summarized graphically in Figure 1. The range of wave-lengths is so great that a logarithmic scale is required. A doubling of the wave-length is called an octave, a familiar term in music. The diagram of the electromagnetic radiations covers about sixty octaves, and of these, only one represents the radiations which are visible. In certain regions, as between the Hertzian and the infrared regions, an overlapping of the radiation known by various names, is indicated. This means merely that radiations of wave-lengths included in the region of overlapping have been produced by the methods which are usually employed for the production of wave-lengths on both sides of this

¹⁷ Günther, P, *Z. Anorg. Chem.*, **44**, 404 (1931).

¹⁸ Compton, A. H., *Nature*, **135**, 695 (1935). The existence of a shortest possible wave-length of 6.2×10^{-6} A has been assumed by A. March, *Z. Physik*, **108**, 128 (1937).

region. A consideration of the mechanisms by which radiations are produced indicates that the nature of the oscillator bearing the charge, whether it be a coil of wire, a molecule moving as a whole, valence electrons in a molecule or atom, or nuclear electrons, usually determines, although in a very indirect manner, the wave-length of the radiations produced.

It is the wave-length which serves to characterize the nature of a radiation and to indicate its penetrability, chemical and optical properties and utility. The amplitude of the wave (or more accurately, the square of the amplitude) serves to visualize the intensity of the radiation.

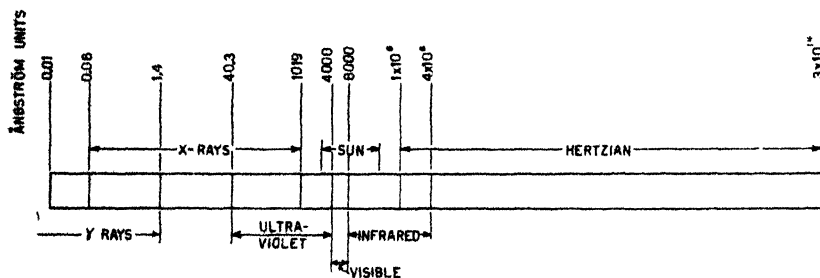


FIGURE 1. Electromagnetic Spectrum.

The impression has been given in the preceding discussion that the wave theory offers an adequate expression of the behavior of radiant energy. It must now be pointed out that there are a considerable number of effects, particularly those concerned with the mechanism of the emission and absorption of radiant energy, for which the wave theory has no ready explanation. These effects are better comprehended on the basis of the quantum theory, according to which quanta or "bundles of energy" are emitted from the source, as explained in the following chapter. The quantum theory may be adequately applied over a considerable field, notably to photoelectric phenomena, Bohr's theory of the atom, and the relationship between the frequencies of lines in emission spectra. Indeed, it has served in the last few years as a great correlating principle for a wide variety of physical properties as diverse as the specific heats of elements and the absorption of radiations.

Great changes in physical theory have arisen from the recent work of De Broglie, Schrodinger and of Heisenberg. Their theories have led to the creation of a new system of mechanics in which the motion of a material particle is always associated with a wave motion, the wave length of which is determined by dividing Planck's universal constant by the momentum of the moving particle. Conversely, in the words of Planck, radiant energy traveling with the speed of light appears on interacting with matter, to "shrink together and concentrate itself at separate points which move like corpuscles, and for that reason are called light-quanta."¹⁰ Each such quantum of radiation is now called a *photon*.

It appears from the newly established points of view that there can be neither pure corpuscular motion nor pure wave motion in physics. Rather, every corpuscular motion is attended by some measure of wave motion and every wave motion involves something of corpuscular motion. The distinction between the

¹⁰ Planck, M., *J. Frank. Inst.*, May 18, July 15, 1927.

two is only gradual and quantitative. The acceptance of such an unlooked-for conception has followed from the experiments of Davisson and Germer²⁰ which, by revealing the diffraction of electrons, demonstrated the motion of even these minute particles to be such as to imply a wave-nature for them.

On the other hand, the elementary quantum plays no part in the equations of Maxwell for radiant energy, which have not been invalidated in even the finest interference measurements. At present, therefore, physicists and photochemists employ both the wave and the quantum aspects of radiant energy in interpreting their data. Wave-lengths or frequencies are used to designate the quality of a radiation, but in discussing its photochemical effects quantum concepts are necessary.

²⁰ Davisson, C., and Germer, L. H., *Phys. Rev.*, **30**, 705 (1927); Thomson, G. P., *Proc. Roy. Soc.*, **A117**, 600 (1928).

Part I

The Sources of Ultraviolet Radiations

Chapter 2

Mechanism of the Emission of Radiant Energy

The occurrence of a photochemical reaction in the ultraviolet region presupposes the absorption of ultraviolet radiation. An understanding of the mechanism of the reaction involves a knowledge of the processes by which the radiant energy is absorbed by one or more of the reacting substances. Since the time of Kirchhoff it has been realized that absorption of radiant energy is the converse of the process by which it is emitted. Reference to this has been made in the preceding chapter in the discussion of the well-known Fraunhofer dark lines in the spectrum of the sun. Since our present views regarding the interaction of radiant energy and matter were derived chiefly from studies of the manner in which matter emits radiations, it seems logical to describe the emission mechanism of the ultraviolet sources in common use before proceeding to a consideration of the absorption of radiations by substances concerned in chemical reactions.

Illuminating sources consist of some form of matter heated to incandescence, such as the carbon particles in an oil lamp or the luminous flame of a gas burner, glowing calcium oxide in the old limelight, rare-earth oxides in the Welsbach gas mantle, or electrically heated wires glowing in an atmosphere of inert gas. When, as in the first of these, the temperature is relatively low, the color of the rays emitted is a mixture of red and yellow. Sources at higher temperatures emit increasing quantities of blue rays so that the color of the light appears more nearly white. At still higher temperatures increasing amounts of the shorter ultraviolet rays appear.

In 1869, Stefan showed that the total amount of energy emitted by a black body increases as the fourth power of its temperature. Although the term "black body" refers to an idealized concept like that of a perfect gas, Stefan's law applies as an approximation to many substances. In experimental work, it may be approximated by a hollow sphere raised to a suitable temperature. The radiation emerging from a small hole is dispersed by a prism or grating and the intensities of the radiations in the various spectral regions are measured by a thermopile and galvanometer. Data of this sort are shown by the curves of Figure 2 in which the abscissae represent wave-lengths and the ordinates intensities in arbitrary units. Curves for three temperatures are included. They rise with increasing temperature in accordance with the Stefan-Boltzmann law; the areas beneath the curves vary as the fourth power of the temperature.

It may also be noted that as the temperature is increased, the wave-length of the maximum intensity shifts from the infrared region to the visible range. The red just begins to show at a temperature of approximately 1500°Abs. and the maximum lies at approximately 20000Å. At the temperature of the tungsten lamp (2000°Abs.), the maximum is at 15000Å. At solar temperatures (approximately 6000°Abs.), it is in the green region, a considerable proportion of ultraviolet rays also being emitted. Wien's displacement law states that with rising temperature the emission shifts to higher frequencies.

After the establishment of these two laws of radiation, physicists sought a theoretical explanation of the manner in which an increase in the temperature of a substance might cause it to emit electromagnetic waves. Since such waves in the Hertzian region are known to be produced by the oscillation of an electrical charge, it appeared necessary to conceive of some type of charged oscillator either borne

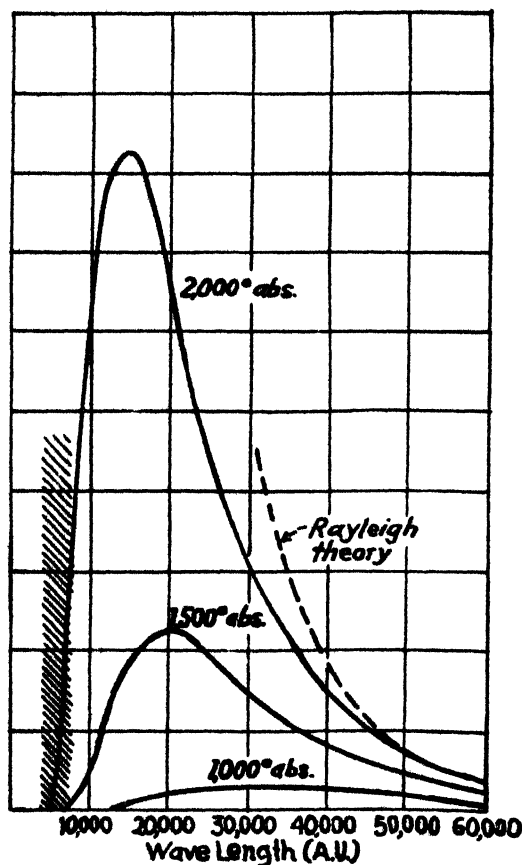


FIGURE 2.

Influence of Temperature on Blackbody Radiation (Eldridge, "Physical Basis of Things," New York, McGraw-Hill Book (c.).

by or located within the atoms of the solid which emits radiations. Mathematical physicists, notably Lord Rayleigh, Maxwell, and Jeans, attempted to develop a theory for the distribution of energy emitted by various hypothetical oscillators, with frequencies dependent upon the temperature. However, these attempts all led to the conclusion that when radiant energy is in equilibrium with matter, the total amount of radiant energy per unit volume should be infinite and that most of it should lie in the short-wave region of the spectrum. Actually, the laws of Stefan and Wien show that but a finite amount of radiant energy can be in equilibrium with matter at a given temperature, and that only at high temperatures does much of it lie within the ultraviolet.

This impasse was overcome by Planck,¹ who in 1900, advanced a theory of radiation in which the motion of hypothetical oscillators could be made to account for the radiation of energy in the amounts and wave-length distribution required by the laws of Stefan and Wien. Its acceptance was delayed because, in his derivation, Planck had been obliged to make certain assumptions at variance with the dynamics based upon Newton's laws of motion. The assumption was made that the energy of a vibrator in the heated body is increased only by jumps as the temperature is increased. These discontinuous increments of energy were called quanta and led to the name of quantum theory for the new viewpoint.

The investigations of Einstein² on the photoelectric effect did much to secure acceptance for the quantum theory, since they demonstrated the existence of discontinuities in the interaction of matter and radiant energy. Additional justification for the adoption of the radical concept of a discontinuity in the energies associated with matter in motion came in 1912 from a field of physics at first sight far from that of radiation when Debye³ successfully applied the quantum theory to the study of the specific heat of solids. Perhaps the greatest factor which contributed to the present general acceptance of the quantum theory was the success of the work of Bohr on the interpretation of spectra, which was founded upon that theory.

It is the purpose of this chapter to acquaint the chemist who may be untrained in modern physics with that minimum of the newer viewpoint necessary for an understanding of the characteristics of the useful sources of ultraviolet radiations.

To that end, it is necessary first to inquire into the meaning of Planck's assumption. His idea implies that a physical system can exist in only certain discrete energy states. On the acquisition of energy, a system jumps from one to another of these states without passing through a continuous series of intermediate ones. A rotating dumbbell possessing a definite angular momentum can acquire energy and assume a new state of more rapid rotation with greater angular momentum. It is usual to think of it doing so by speeding up through all intermediate speeds of rotation. The quantum theory, however, makes the radical assumption that this is not the case and that, in speeding up, the change in rotational energy is discontinuous. Only certain rotational energies can be possessed by the dumbbell, and when speeding up, it can jump only from one to another of these. At first sight this seems contrary to everyday observation. This is not, however, necessarily the case because the energies possessed by a large object in the permissible states differ so little that the speeding-up process appears to be continuous. Matters are quite different in the case of minute systems such as those of atoms or electrons where the discontinuity of the process dominates the picture. Poincaré has shown mathematically that the fact that the total radiation from a black body at a finite temperature is finite requires that the ultimate motion involved in the mechanism of radiation be in some way discontinuous.

Since the work of Planck, different, and in some respects more satisfactory, derivations of the quantum laws of radiations have been given by Jeans,⁴ by Darwin and Fowler,⁵ and by Einstein.⁶ The last of these, which has led to one of the fundamental laws of photochemistry, requires that the molecules emitting

¹ Planck, M., *Ann. Physik*, **4**, 553 (1901).

² Einstein, A., *Ann. Physik*, **20**, 199 (1906).

³ Debye, P., *Ann. Physik*, **39**, 789 (1912).

⁴ Jeans, Sir J., *Phil. Mag.*, **20**, 953 (1919).

⁵ Darwin, C. G., and Fowler, R. H., *Phil. Mag.*, **44**, 450 (1922).

⁶ Einstein, A., *Physik. Z.*, **18**, 121 (1917).

radiations can exist only in certain definite energy states, and that when a molecule jumps from one state to another the accompanying loss or gain of energy is always one or more complete quanta of radiation, fractions of a photon not being emitted or absorbed.

It is as meaningless to speak of the amount of energy in a quantum without specifying its frequency as it would be for a chemist to speak of the weight of an atom without stating to which element he referred. The magnitude of a quantum of radiation depends upon the wave-length (frequency) of the radiation. The relation between the masses of the atoms of different elements is a complex one, but that between the magnitudes of the quanta of radiations of various frequencies is the very simple one of direct proportionality. The frequency of the radiation multiplied by a constant gives the energy per quantum of that radiation. In most physical literature the frequency is denoted by the Greek letter ν and the constant by h . Therefore, the energy ϵ of a photon of radiation of a given frequency ν is given by

$$\epsilon = h\nu$$

This means that the constant h can be expressed by $h = \epsilon \times \frac{1}{\nu}$, that is, energy multiplied by the reciprocal of a frequency, which is the period or time of a vibration. The unit in terms of which h is measured is then one of energy multiplied by time, or erg seconds. The value of h has been determined by many methods to be 6.55×10^{-27} erg sec. The erg second is called by physicists a unit of action, this term being used to denote the product of energy and time.

When the quantum constant h is multiplied by the very large number which expresses the frequency of green light, the resulting energy is found to be still a small number, 3.93×10^{-12} erg. This is nevertheless of such an order of magnitude that its effects in producing discontinuities in radiation are discernible by physical methods. The quantum of energy associated with a line at 5890Å would be 1.6×10^{-16} erg greater than that associated with one at 5891Å.

CONTINUOUS AND LINE SPECTRA

The spectrum produced when the radiation emitted by a glowing solid is passed through a prism blackens a photographic plate continuously and rather uniformly. An additional effect is produced when gases or vapors at high temperatures emit light. In 1829, Sir John Herschel examined the spectra of the colored light produced by heating certain salts in an alcohol flame and found the emitted energy to appear concentrated in lines corresponding to relatively few wave-lengths. Such spectra are called line spectra, or discontinuous spectra. The wave lengths at which such lines occur characterize the elements the vapors of which produce them when heated. Bunsen and Kirchhoff employed these bright-line spectra in the detection of those elements which emit lines under these conditions. In the preceding chapter, it was noted that the Fraunhofer black lines which cross the spectrum of sunlight are due to the absorption of certain lines by elements present in gaseous form in a layer surrounding the sun. The positions of these black lines on the wave length scale correspond to the positions of the bright lines emitted by the same elements when heated and viewed directly. The identification of the Fraunhofer lines with those emitted by elements in the laboratory provided the means by which it became possible to determine which elements are present in the reversing or absorbing layer of gas surrounding the sun.

The bright line emission spectra of the elements consist, when viewed through

a spectrograph, of a series of lines separated by regions of comparative darkness. They are produced as the result of processes occurring in widely separated atoms or molecules of substances in the vapor or gaseous state. The same processes occur also in the atoms or molecules comprising incandescent solids, but in this case any natural frequencies of rotation or vibration associated with these atoms or molecules are masked by effects produced by the continuous bombardment of neighboring atoms or molecules. The result is that the spectrum is continuous and yields no information in regard to the nature of the atoms or molecules present in the incandescent solid. As indicated in Figure 2, the predominating frequency is, instead, a function of the temperature. Some exceptions to this statement may be noted. The rare earths used in the Welsbach gas mantle, when heated to incandescence, emit line spectra. Nichols⁷ described ten or more crests on the brightness curve of glowing neodymium oxide, which, however, bear no relation to the true line emission or absorption spectra of this compound. The theory of the origin of this type of spectrum has recently been discussed by Van Vleck.⁸ Grain size influences the nature of the temperature radiation from other metallic oxides.⁹

Just as certain incandescent solids give indications of line spectra superposed on their continuous radiation, so conversely gases or vapors produce beneath their characteristic line spectra a more or less faint continuous background. Its origin has been attributed to the effects of free electrons of varying kinetic energies joining with ions to produce atoms or, in the case of molecules, to recombination of free atoms possessing varying kinetic energies. (See Chapter 9.)

There are two kinds of line spectra, those emitted by atoms and those emitted by diatomic or polyatomic molecules. The latter spectra, *i.e.*, molecular spectra, were called band spectra by the earlier spectroscopists whose apparatus of low resolving power revealed them only as a number of bands of light and darkness often overlapping to produce a channeled or fluted appearance. With more modern equipment they have been resolved into groups of lines. Molecular spectra will be reserved for discussion in Chapter 13; the remainder of the present chapter will be devoted to a consideration of the order underlying the positions of the lines in atomic spectra, and the theories of the mechanism of emission of radiation which have been devised to account for it.

The photochemist needs to know something of the theory of line spectra for two reasons. In the first place, his sources of radiation are predominantly means for treating gases or vapors of elements so that they emit line spectra. (In most sources the line spectra are somewhat complicated by the incidental production of some molecular spectra.) The lines which carry the radiant energy are at first sight spaced quite at random, and the intensities of different lines vary greatly in an apparently irregular manner. If it is desired to carry out a reaction by energy of wave-lengths between 2500 and 2600 Å, it is necessary to know which sources emit line spectra having strong lines located within this region. If, on the other hand, one wishes to test the action of the region of 2800-2900 Å, a source must be chosen having strong lines in that region, and only faint ones, if any, in the 2500-2600 Å region.

In the second place, the photochemist must understand the process by which molecules absorb energy. Since this is the converse of the process by which they emit molecular spectra and is quite complicated, it may best be approached after

⁷ Nichols, E. I., *Proc. Nat. Acad. Sci.*, **11**, 47 (1925); *Chem. Abs.*, **19**, 1376 (1925).

⁸ Van Vleck, J. H., *J. Phys. Chem.*, **41**, 67 (1937).

⁹ Liebmann, G., *Z. Physik*, **63**, 404 (1930); Skaupy, F., *Physik. Z.*, **28**, 842 (1927).

to one, the equation yields a series of lines in the ultraviolet. Most lie far out in the difficultly accessible region; they were discovered by Lyman.

THEORY OF THE MECHANISM OF THE EMISSION OF LINE SPECTRA

The Hydrogen Spectrum. The fact that the frequency of a spectral line is related to the difference between two terms was long a source of difficulty to the theorists who conceived of the spectral frequencies as in some manner related to natural frequencies of intra-atomic vibrations. The spectra of more than twenty elements had been resolved, at least in part, into series when Bohr in 1913 successfully employed the quantum theory of Planck in accounting for the origin of the lines in series spectra of the elements. He applied the new and almost unaccepted idea of the discontinuity of "action" to the dynamics of the structure of the atom as pictured by Lord Rutherford. In Rutherford's theory an atom is composed of a central positively charged nucleus around which there revolve in closed orbits as many electrons as are required to balance the positive charge of the nucleus. The positive charge of the nucleus as well as the number of electrons is equal to the atomic number of the element. The hydrogen atom consists of one electron revolving around a nucleus of equal and opposite charge. In helium, there are two revolving electrons, in lithium three, in carbon six, and so on to uranium with 92 electrons.

Although the orbits of the electrons are conceived as elliptical, it is perhaps simpler to regard them as circular in an introductory consideration of the theory as it applies to hydrogen. The electrostatic force of attraction between the electron and the oppositely charged nucleus balances the centrifugal force of rotation of the electron and so holds it in its orbit. A difficulty arises when the radiation of energy by such a system is considered. Motion in a circle is accelerated motion. It is fundamental in electrodynamics that an accelerated charge radiates energy, and the electron would be expected to spiral in gradually toward the nucleus. Actually, however, the spectroscopist knows that an atom emits no measurable radiation unless energy is supplied to it in some manner as by mechanical impact, by heat or by an electrical discharge.

The discrepancy between the experimental results and those expected on the basis of electrodynamics was as serious as that encountered in the study of black body radiation, which Planck had met by making the radical assumptions of the quantum theory. Bohr met the difficulty in the same manner by adopting the theory of Planck. He assumed it possible for the electron of the hydrogen atom to revolve, without radiating energy, in certain discrete orbits in which its angular momentum mvr (m is the mass of the electron, v its angular velocity, and r the radius of the orbit) is an integral multiple of $h/2\pi$, that is, $nh/2\pi$. By using known values of the mass and charge of the electron, it was possible to calculate from this quantum condition and an equation relating the centrifugal force and the electrostatic force between the electron and the nucleus, the radii of the orbits in which the electron could move without radiating energy. These were found to have radii of 0.5, 2.0, 4.5 and 8A, when n , called the quantum number, had the successive values 1, 2, 3 and 4. The radii of the permitted orbits increase as the squares of the quantum numbers. Each such orbit represents a state in which the hydrogen atom possesses a calculable amount of energy. Thus the atom may exist in definite energy states, or may be said to possess definite energy levels.

Bohr assumed that energy is radiated only during the time in which the electron falls from an orbit in which the atom has greater energy to one in which it has lesser energy; that is from an outer to an inner orbit. The energy emitted is the

difference between the energies possessed by the atom in the initial and final states. The transition may be either between adjacent or more widely separated permissible orbits or energy states. In terms of the quantum theory, the energy radiated is expressed by $h\nu$. Therefore, the difference between the energies in the initial and final states when divided by h yields the frequency of the line emitted.

It appears, therefore, that in the Bohr theory the frequency of the emitted line is not directly related to that of any vibration in the atom before or after emission, but to a difference between the energies possessed by the atom before and after emission. Emission from an atom persists for but a very brief period. The persistence of the lines seen to be emitted from a discharge tube is due to the successive emissions of the line by different ones of the great number of atoms in the tube. Of these, some at a given moment are in the resting state, others are being excited by the electrical discharge as a preliminary to emission, others are in the excited state in which the atom holds the energy acquired during excitation, and still others are emitting the observed line. Bohr's theory affords an explanation of the fact that in the Rydberg formula the wave-number of the emitted line is represented as the difference between two terms.

In terms of this theory, the various sources of ultraviolet light are devices for introducing energy into atoms (or sometimes molecules) in order to raise them to higher energy levels. This process is called excitation. In the Bohr picture, this consists of shifting an electron from an inner orbit, in which its potential energy has the greatest negative value, to an orbit of greater radius. The excited atoms have but a very transient existence, usually of the order of 10^{-8} second, after which the electron drops to an orbit of lower energy, which may or may not be the innermost orbit. It is during this process that a spectral line is emitted.

A transition of an electron from the second to the first energy level is accompanied by the emission of the first line of the Lyman series of hydrogen lines in the ultraviolet. An atom in which the electron transition is from the third to the first energy level emits the second line, one from the fourth to the first level emits the third line, and so on. The differences in energy in the successive energy levels lessen as n becomes large. Therefore, the differences between these higher levels and the resting level differ less and less as n becomes large and the successive lines of higher frequency occur closer together as the limit for infinite n is approached.

It is by no means always the case that the electrons fall back from higher levels to the resting level or innermost orbit. When they fall back only to the second level, the lines of the Balmer series are produced. Transitions to the third level gives the lines of the Paschen series. These statements follow directly from the Rydberg formula, the number used for n_1 giving the orbit to which the electrons drop during emission.

It may not be apparent why thirty or more lines of the Balmer series are seen simultaneously in the emission from a discharge tube. In any source there is present a tremendous number of atoms, some moving with high and some with low velocities, and others at rest. When such a mass of atoms is excited by the passage of an electrical discharge, there are differences in the states of excitation attained by different atoms. Some are excited to the second, and others to various other energy levels, even very high ones. Each atom then emits in a manner depending upon its state of excitation. When the radiation from the whole collection of emitting atoms is viewed through a prism, the lines resulting from each of the many types of transition in progress in different atoms are seen simultaneously. The relative intensities of the lines are related to the probabilities

with which the excited states giving rise to the lines are produced under the experimental conditions of excitation.

Elements Other Than Hydrogen. In the case of other elements, the line spectra are much more complex. In the iron spectrum, there are thousands of finely spaced lines. King¹⁰ has recorded more than 3000 lines in the cerium spectrum, 1600 of which lie between 3000 and 4700 Å.

In the case of the spectra of the alkalis, it was found possible to classify the lines, at first by their distinctive appearances, into four series. Three of these were named by Rydberg the principal, sharp and diffuse series. A fourth series, discovered by Bergman in the infrared region, was called by Hicks the fundamental series, for reasons no longer pertinent. The descriptive significance of these names is not maintained in the case of more complex elements but because of their historical significance they have been generally retained and their abbreviations, P, S, D and F, are in common use in the designation of spectral terms.

The Rydberg formula for the frequencies of the lines of a series for the alkalis differs from the simplified form applicable to hydrogen in having two additional constants, μ_1 and μ_2 :

$$\nu = R \left(\frac{1}{(n_1 + \mu_1)^2} - \frac{1}{(n_2 + \mu_2)^2} \right)$$

These constants have fractional values characteristic of the elements. These differ also for lines of the sharp, principal, diffuse and fundamental series of a given element. In the case of sodium, when μ_1 is 0.626 and μ_2 is 0.13, the expression, using $n_1 = 1$, gives the lines of the principal series. If n_1 is taken as 2 and the μ_1 and μ_2 values are reversed, the lines of the sharp series are given. By replacing μ_2 by a new constant, $\mu_3 = 0.99$, in the second term, the lines of the diffuse series are obtained. By making $\mu_1 = 3$, using μ_3 in the first term and still another constant $\mu_4 = 0.999$ in the second term, the infrared lines of the Bergman or fundamental series are found. These four constants, known also as "defects," are only approximations, and the lines are never given as exactly as is the case with the simplified expression for hydrogen in which "defects" may be neglected in all but the most accurate work.

The existence of these "defects" and the resulting occurrence of lines of sharp, diffuse, principal and other series, implies that the energy states of the alkali atoms cannot be sufficiently characterized by the single quantum number n . A second number L is required to distinguish the energy levels which exist. In the earlier development of the theory it was assumed that this was due to the fact that the orbits were elliptical rather than circular. Electrons moving in such orbits would have, in addition to a rotary motion about the focus at which the nucleus is situated, a radial motion toward and from the nucleus. For each of these forms of periodic motion quantized energy states were postulated. This increased the number of energy levels, since for each n value there may be several L values. In general, the energy differences between L states with the same n value are less than those between the states with successive n values. It has been found that L , called the orbital quantum number, may have the value zero, or any integer up to one less than the value of n .^{*} An energy level or term for

¹⁰ King, A. S., *Phys. Rev.*, **29**, 366 (1927).

^{*} It is unnecessary to discuss in detail the history of the development of the theory of these quantum numbers or of others since introduced. They were first arrived at by an extension of the Bohr theory by Sommerfeld, but have subsequently been found to emerge naturally from the theories of quantum mechanics.

which L is zero is an S term, one for which it is 1 a P term, one for which it is 2 a D term, and one for which it is 3 an F term.

As in the case of the Bohr theory of the hydrogen atom, the spectral lines result from transitions from higher to lower energy levels. Not all of the theoretically possible transitions between terms are found to occur under the usual experimental conditions, or, as the spectroscopist would express it, not all terms combine to give lines. It has been found possible to predict which transitions may occur by the aid of certain *selection rules*. These were originally obtained empirically, but have since been found to have a theoretical basis. One selection rule states that, in absorption or emission, L must increase or decrease by one. In other words, transitions may occur only between states whose L values differ by but one unit. S states can undergo transitions only to or from P states, but P states may combine with either S or D states, D states with P or F states, and so on. Other transitions are said to be forbidden. Selection rules are not, however, absolutely binding, since under certain conditions, lines corresponding to transitions other than those given by the rules may appear with low intensities. Thus, the term *forbidden* is a misnomer, since forbidden lines are really lines corresponding to transitions of only low probability. The quantum mechanics affords methods for calculating the probability of transitions.

There is no selection rule limiting the number of integers by which the principal quantum number n may change in a transition.

Spectroscopists denote a spectral line by writing the terms separated by a dash. In writing the terms the abbreviations S , P , D , etc. are used to indicate the L value of each; these are preceded by numerals for the n value of each. Thus a line of the principal series may be written $1S-2P$, or in general, $1S-nP$, successive values of n giving the successive lines of the series. Lines of the sharp series are given by $2P-nS$, those of the diffuse series by $2P-nD$, of the Bergman series by $3D-nF$. The symbol of the last term refers to the series of which the lines are members. The first term gives the limit of the series. The sharp and diffuse series of lines of the alkalis approach the same limit, depending upon whether L increases or decreases by one in falling from a state of greater to one of lesser energy.

Further complications arise when the processes of emission or absorption occur in a magnetic field. Under these conditions, a given line may be split into several lines (Zeeman effect). Even without the application of a magnetic field, certain lines of the alkalis, *e.g.*, the D line of sodium, may be observed to be resolved by a spectroscope into two closely adjacent lines, called a doublet. In the case of elements of other groups of the periodic system there may be triplets, quadruplets and even higher degrees of multiplicity, thus greatly complicating the spectra. In some cases, the corresponding lines of multiplets may not lie close together but may be hundreds of Ångstrom units apart and be separated by great numbers of intervening lines.

These effects may be accounted for by considering that the terms are split into others of but slightly different energy levels. Thus, to characterize the greater number of terms implied, a third quantum number, J , called the inner quantum number, is employed. In writing the terms, the value of J is placed as a subscript to the right, as in $1S_{1/2}$, $2P_{3/2}$, etc. The multiplicities of the terms are indicated by upper left indices, as in 3D_2 .¹¹ A selection rule states that J may either increase

¹¹ For a discussion of this notation, see Russell, H. N., Shenstone, A. G., and Turner, L. A., *Phys. Rev.*, **33**, 900 (1929).

or decrease by one, or need not change in a transition, except that in cases in which it is initially zero, it must change.

The multiplicities exhibited by an element depend upon its position in the periodic table and must, therefore, be related to the electronic configuration of the atom. The terms of atoms with an even number of electrons have odd multiplicities. Those of atoms with an odd number of electrons have even multiplicities. Elements of the alkalis have doublets, those of the alkaline earths singlets and triplets, those of the next group doublets and quartets, and those of the next group singlets, triplets, quintets, etc.

Many attempts have been made to arrive at a physical interpretation of these features of the spectral terms by extending the Bohr theory to atoms having more than one electron. These take into account the interactions between the electrons, and involve complexities of interest chiefly to the specialist in atomic spectra.¹² It need only be mentioned here that this development showed the need of a new concept—the electron spin—introduced by Uhlenbeck and Goudsmit¹³ and by Bichowsky and Urey.¹⁴ This assumes each electron to rotate about its own axis besides moving in an orbit about the nucleus.* The electron spin has an angular momentum $1/2 h/2\pi$.

The effects of the spins of the electrons in the atom (only the valence electrons or those outside the kernel need be considered) may be lumped together by the methods of vector analysis into a resultant spin vector S for the atom. This assumes only certain discrete values. If all the spins are parallel, S is equal to one-half the number of electrons since each contributes $1/2$. The contributions of antiparallel electrons neutralize each other. For example, if as in the alkaline earths, there are two electrons outside the kernel, S will be one if the spins are parallel and 0 if they are antiparallel. The extreme values which the quantum number J may possess for a given L level for a given atom are obtained by adding L and S and by subtracting S from L . J may also have all intermediate values which differ from these extreme values and from each other by integers. This means that if L is greater than S , the number of J values for a given L (the multiplicity of the term) is given by $2S + 1$.

It must now be emphasized that the Bohr theory, although useful in stimulating the earlier development of the theory of spectra, had many arbitrary features and, indeed, probably was in error in certain features. The quantum numbers and selection rules have subsequently been shown to emerge more logically from quantum mechanics. The methods employed require a degree of mathematical

¹² For accounts of these see books on atomic spectra. The following have been consulted in preparing this brief summary: Johnson, R. C., "Spectra," London, Methuen, 1928; Herzberg, G., "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937; White, H. L., "Introduction to Atomic Spectra," New York, McGraw-Hill, 1934; Candler, A. C., "Atomic Spectra and the Vector Model," 2 Vols., Cambridge Univ. Press, 1937. An exhaustive bibliography has been given by Gibbs, R. C., *Rev. Modern Physics*, 4, 278 (1932).

¹³ Uhlenbeck, G. F., and Goudsmit, S., *Naturwiss.*, 13, 953 (1925), *Nature*, 117, 264 (1926); see also Compton, A. H., *J. Frank. Inst.*, 145, 1921, Aug.

¹⁴ Bichowsky, F. R., and Urey, H. C., *Proc. Nat. Acad. Sci.*, 12, 80 (1926).

* The state of each individual electron in an atom can be described by four quantum numbers, n the principal quantum number, l the orbital quantum number, m_l the magnetic quantum number, and m_s the electron spin number. n can have any integral value, l can have any integral value up to one less than n , m_l may have any integral value between l and $-l$, including zero, (or a total number of possible values equal to $2l + 1$), and m_s can have only the values $-1/2$ or $+1/2$. Pauli's exclusion principle states¹⁵ that no two electrons in the same atom can have all four quantum numbers the same. This principle and the restrictions on the values which the quantum numbers may possess permit the description of the electron configurations of the atoms of all the elements of the periodic table. Fowler states¹⁶ that it is possible to predict from the electron configuration of an element, however complex, the main features of its spectrum.

¹⁵ Pauli, W. Jr., *Z. Physik*, 31, 765 (1925).

¹⁶ Fowler, A., *J. Chem. Soc.*, 1928, 777.

training possessed by relatively few chemists and must be sought in special texts. This development has arisen from the work of Heisenberg¹⁷ on matrix mechanics and independently from the introduction by Schrödinger¹⁸ of the wave equation of De Broglie¹⁹ into the classic equation for the propagation of elastic waves. The result of the latter approach was a differential equation which could be applied to the motion of the electron in the hydrogen atom. This equation has a discrete set of solutions called *eigenfunctions* which represent energy states of the atom. According to these theories, the electron orbits of the atom have lost their once-assumed definiteness and it is possible only to calculate the probability of an electron being found within a definite minute volume of space. They do, however, confirm the existence of definite energy levels, transitions between which give rise to the spectral lines. Indeed, it may be said that although the Bohr theory had assumed their existence, their occurrence was nevertheless inexplicable and, until the advent of the quantum mechanics, marked a sharp break with all previous conceptions of electrodynamics.

Experimental data confirming the existence of definite atomic energy states are now abundant. The stepwise excitation of atoms by the impacts of electrons carrying definite amounts of kinetic energy was mentioned in Chapter 1. This stepwise production of various spectral lines in succession has, since the pioneering experiments of Franck and Hertz, been carried out in the case of many elements. For example, Schulze²⁰ has excited argon in seven stages. The method offers great experimental difficulties and the literature contains many discrepancies in the values assigned to the various resonance potentials of the elements by modifications of this method.

The various spectral lines or groups of lines may be also produced in an analogous step-wise manner by carefully controlled thermal excitation of the elements. In the Pasadena laboratory of the Mt. Wilson observatory, King volatilized the metals in a graphite tube electrically heated in a specially designed furnace to temperatures not far below that of an electric arc. He showed²¹ that calcium vapor yields a line at 4227Å at relatively low temperatures, and that lines at 3969 and 3934Å appear only at temperatures above 2400°C. He has also given²² temperature classifications of the lines of strontium, barium, magnesium, iron, titanium, vanadium, chromium, cobalt, nickel, manganese, scandium and many other elements. In the case of iron, he has grouped 902 lines according to their occurrence or absence when the temperature is 1600-1700°C., 2000°C., or 2500-2600°C. Only eleven lines are emitted at 1400°C. The method, which has also been employed by others,²³ is chiefly of value to the spectroscopist as an aid in classifying the lines into various series.

PRODUCTION OF IONS IN ULTRAVIOLET SOURCES

The chemist is familiar with ions produced as the result of electrolytic dissociation in aqueous solutions. The physicist, however, frequently encounters ions in the gaseous state, since by the application of high temperatures, electric dis-

¹⁷ Heisenberg, W., *Z. Physik*, **33**, 879 (1925).

¹⁸ Schrödinger, E., *Ann. Physik*, **79**, 361, 489, 734 (1926); *Phys. Rev.*, **28**, 1049 (1926).

¹⁹ De Broglie, L., *Phil. Mag.*, **47**, 446 (1924); *Ann. de Phys.*, **3**, 22 (1925).

²⁰ Schulze, B., *Z. Physik*, **56**, 378 (1929).

²¹ King, A. S., *Astrophys. J.*, **28**, 389 (1908); **29**, 381 (1909).

²² *Ibid.*, **29**, 190 (1909); **48**, 13 (1918); **51**, 179 (1920); **37**, 239 (1913); **56**, 318 (1922); **39**, 139 (1914); **59**, 155 (1924); **41**, 86 (1915); **60**, 282 (1924); **42**, 344 (1915); **53**, 133 (1921); **54**, 28 (1921); **65**, 86 (1927); **69**, 377 (1939).

²³ Paton, R. F., and Rassweiler, G. M., *Phys. Rev.*, **33**, 16 (1929); Ritschl, R., *Ann. Phys.*, **13**, 337 (1932); Schüler, H., *Z. Physik*, **37**, 728 (1926).

charges or certain radiations, it is possible so strongly to excite an atom that one or more of its electrons is sent to an orbit extremely far from the nucleus. Since the attractive force of the nucleus becomes insufficient to hold the electron in a far distant orbit, it becomes lost to the atom, and shoots out into space where, as a minute particle, it behaves as an independent unit, and is one of the particles making up an "electron gas." The atom which has lost the electron or electrons is called an ion.

The work necessary to remove an electron from an atom is greater than that required to displace it to any of the hypothetical orbits representing the stationary energy states of the atom. It is the ionizing work; when expressed in electron-volts, commonly shortened to volts, it is called the ionization potential. It is greater than any of the potentials corresponding to the excited states. In the case of mercury, it is 10.4 volts.

To ionize an already excited atom requires less work than is needed in the case of an atom in its stable state. To ionize a hydrogen atom which is already excited to a high energy level requires less energy than to ionize one excited only to a lower energy level. The difference between the amounts of energy required for ionization in these two cases represents the amount of energy required to raise the atom from the lower to the higher stage of excitation. This would be the amount of energy emitted in a spontaneous return of the atom from the higher to the lower energy level. By multiplying the frequency of the emitted line by the Planck constant, the value of this energy is obtained in ergs.

By both the spectroscopic method and the method of studying the effects on atoms of impacts of electrons accelerated by electric potential gradients, physicists have obtained a large amount of information regarding the energies required to excite atoms of most of the elements to various energy levels, or to ionize them. The detailed results have been summarized by Bacher and Goudsmit.²⁴ The ionization potentials of a few of the elements most frequently employed in sources of ultraviolet rays are given in Table 1, which also includes for some a resonance potential and the energy required to expel a second electron from an ion of the atom.

Table 1.—Resonance and Ionization Potentials of Various Elements.

Element	Resonance Potential (volts)	Ionization Atom. ————— (volts) —————	Potentials of Ion —————
Hydrogen	10.4	13.5
Helium	20.4	24.46
Carbon	11.2	24.3
Nitrogen	8.2	14.5	29.5
Neon	11.8	21.5	40.9
Sodium	2.1	5.1
Argon	13.2	15.7	27.8
Mercury	4.9 (6.67)	10.38	18.65

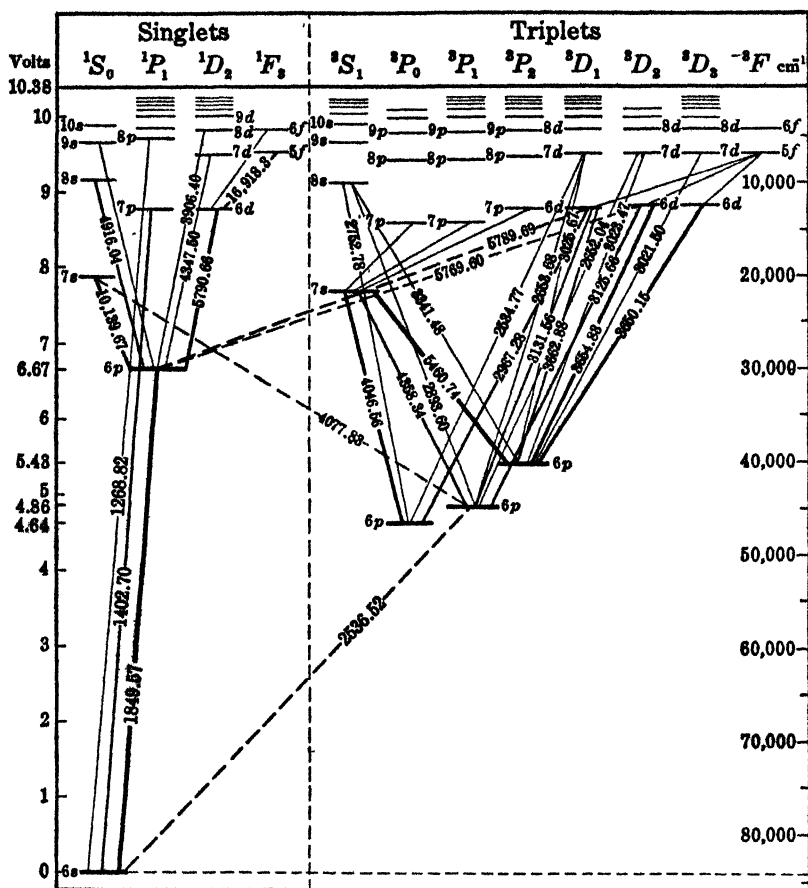
Energy-Level Diagrams. The transitions permissible between the energy states of an atom are most readily set forth in diagrams called energy-level diagrams or Grotrian diagrams.²⁵ These serve also to indicate the energies in the various levels. Such a diagram for mercury is given in Figure 4.

A horizontal line at the top of the diagram represents the energy of the ion,

²⁴ Bacher, R. F., and Goudsmit, S., "Atomic Energy States," New York, McGraw Hill Book Co., 1932.

²⁵ Grotrian, W., "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," 2 vols., Julius Springer, Berlin, 1928.

which is arbitrarily taken as zero. A dot placed near the bottom of a vertical line at the left of the diagram indicates the energy of the stable or normal state of the atom. The distance at which it is located below the zero energy state of the ion on a suitable scale represents the energy which must be put into the atom to ionize it. Since the atom in its normal state has less energy than the ion, which is arbitrarily taken as zero, the energy associated with the atom or with any state of excitation less than ionization, is considered to have a negative value. The energy values are frequently expressed in electron-volts, since in many cases the



of light converts these frequencies into the more convenient wave-numbers. Usually, the levels are determined spectroscopically by multiplying the wave-number of the line by hc to obtain the increment of energy between the energy levels.

Energy-levels for each of the S, P, D and F terms are designated by short horizontal marks. Doublets, triplets, etc. are indicated by using separate columns for each member of the multiplet. The state of excitation for each electron is usually denoted by giving the principal quantum number as a numeral for each short horizontal line marking an energy state.

Diagonal lines are drawn connecting the various states in accordance with the selection principles. The difference between the wave-numbers of the states connected by a diagonal line yields the wave number of the spectral line. Transitions between terms of unequal multiplicity are called intercombination lines. They violate the selection rule that when J is 0, its value must change. It happens, however, that the prominent mercury resonance line, 2537A, is such an intercombination line.

Chapter 3

Survey of Sources

The various sources of ultraviolet radiations are all devices for the application of energy to atoms and molecules, usually in the vapor or gaseous states, for the purpose of exciting them to higher energy-levels. The differences between the many types of apparatus lie in the choice of the atoms which are excited, in the form of energy applied for the excitation, and in the means adopted for its application.

Once the excitation has been effected, the excited atoms or molecules retain their increments of energy for a brief period and then revert to states of lower energy, emitting their extra energy as radiation. The duration of the excited states may be altered somewhat by varying the pressure of the gas or by adding an inert gas.

The natural source of radiations, the sun, is discussed in Chapter 11, following a consideration of filters, since atmospheric filtration prevents some of its radiations from reaching the surface of the earth. The most important artificial sources of ultraviolet rays are the arc, spark and glow discharge. In the following paragraphs the chief points of distinction between these types of discharge will be described, after which other less widely used sources will be considered.

The passage of a direct current discharge through gases at low pressures frequently gives rise to the glow discharge, the well-known phenomenon observed in a Geissler tube. In it, various parts of the tube assume characteristic appearances known as the cathode glow, the Crookes dark space, the negative glow, the Faraday dark space, the positive column and, when present, the anode glow.

The arc is a discharge of electricity through a gas, which may be at any pressure, under conditions such that one or both of the electrodes becomes heated and by vaporization contributes a stream of gaseous material which aids in the conduction of the current (direct or alternating) across the space. In these two forms of discharge—the glow and the arc—the impressed voltage is usually low, as compared with the very high voltages employed for the spark discharge. In the arc, the potential drop in the region of the cathode is usually very low, of the order of tens of volts, but in the glow, it is of the order of hundreds of volts. In practice, the spark usually involves the very brief oscillatory discharge of some form of condenser across an air-gap, with the production of light and heat. With suitable equipment, a series of very rapidly repeated discharges may occur with the production of a loud sound.

Close to the cathode in a glow discharge in nitrogen at 0.5 mm. pressure¹ is a narrow dark space (Crookes dark space), followed by an intense negative glow region which decreases in intensity to the Faraday dark space, several times wider than the cathode dark space. This is followed by the bright positive column which begins sharply at a definite position and extends, usually with uniform intensity, toward the anode. Under certain conditions, the positive column may be striated. There may also be an anode glow. The positions between the

¹This discussion of the glow discharge is based upon one by Dushman, S., *Elect. Eng.*, **53**, 1204, 1283 (1934); see also Found, C. G., *Trans. Illum. Eng. Soc.*, **33**, 161 (1938).

boundaries of these various regions are determined by the cathode, since they are changed if the cathode is moved within the discharge tube but are not affected by moving the anode. If the anode is made to approach the cathode, the length of the positive column decreases. It is possible to eliminate the latter completely and have the anode located within the negative glow or in the cathode dark space.

The potentials with respect to the cathode at various points may be determined by the use of exploring wires or electrodes introduced into the various regions, a method employed by Stark, Retschinsky and Shaposchnikoff² and placed upon a sound theoretical foundation by Langmuir and Mott-Smith.³ The use of this "probe" method has been of great value in advancing our knowledge of the mechanisms occurring in gaseous discharges, as it is capable of yielding information as to the potential distribution, the densities of ions and the mean kinetic energies of the free electrons.

Close to the cathode is a narrow region in which there is a steep potential gradient, the drop varying from 60 to 400 volts, depending on the nature of the gas and the cathode. Much of the entire discharge voltage drop occurs in this region. In the Faraday dark space there may be a slight positive or even a negative gradient. Throughout the positive column, the gradient is constant, so that the total voltage drop in the tube depends upon the length of the positive column as well as upon the cathode fall. In the glow discharge, there is little change in voltage at the anode. Compton and Morse⁴ assume the large amount of energy consumed in the cathode fall to be used in accelerating positive ions toward the cathode. By bombarding the cathode, these liberate electrons; the liberated electrons while close to the cathode receive enough energy to enable them on striking atoms to produce more positive ions, and so continue the process. These authors calculate that an electron makes about ten such ionizing collisions in passing through the region of the cathode fall, and consider that most of the current at the surface of the cathode is carried by positive ions.

The large drop of 300 or more volts in this region may be lessened by employing some accessory method of inducing the cathode to emit electrons, such as heating it to produce thermionic emission or irradiating it with ultraviolet light to cause photoelectric emission. By such methods the cathode drop may be reduced to a value related to that of the ionization potential or of a resonance potential of the gas.

The remaining space between the electrodes is called the plasma, a term also used in the case of arcs. Langmuir⁵ showed that the thickness of the cathode sheath is of the order of 0.01 mm. Electrons from the cathode are accelerated in this sheath and carry their energy into the plasma where most of the emission of light occurs. Electrons which have acquired the energy of the cathode drop V_c (electron-volts) are called primary electrons. Such a primary electron on striking a gas atom may lose to it by inelastic impact the energy required for ionization, V_I . It then has left the energy $V_c - V_I$ and is called a secondary electron. Its energy may still be sufficient to excite certain atoms, depending upon their resonance

² Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann. Physik*, **18**, 213 (1905).

³ Langmuir, I., and Mott-Smith, H. J., *Gen. Electric Rev.*, **27**, 449, 538, 616, 762, 810 (1924). For recent developments of the theory of the probe method, see Davydov, B. I., and Zmanovskaya, L. I., *J. Tech. Phys. (U.S.S.R.)*, **6**, 1244 (1936); Emeleus, H. J. and Brown, W. L., *Phil. Mag.*, **22**, 898 (1936); Polin, V., and Gvozdozer, S., *Physik Z. Sowjetunion*, **13**, 47 (1938); *Chem. Abs.*, **32**, 4422 (1938); Yankin, G. M., *J. Tech. Phys. (U.S.S.R.)*, **8**, 45 (1938), *Chem. Abs.*, **32**, 5692 (1938).

⁴ Compton, K. T., and Morse, P. M., *Phys. Rev.*, **30**, 305 (1927). For recent observations on the cathode region, see Brewer, A. K., and Westhaver, J. W., *J. Applied Phys.*, **8**, 779 (1937); Güntherschulze, A., and Betz, H., *Z. Physik*, **108**, 780 (1938).

⁵ Langmuir, I., *Phys. Rev.*, **33**, 954 (1929).

potentials. When the electron after such collisions no longer has enough energy to excite atoms by impact, it is called an ultimate electron.

Although in this discussion, it has been assumed that the cathode is cold and need not contribute any metallic vapor to the glow, it is possible under certain conditions to have a glow discharge from a molten cathode. Although the glow form of discharge is most commonly produced in gases at low pressures, nevertheless it may be produced under some conditions at atmospheric pressure if the current carried by the discharge is kept at only a few milliamperes. As the current is increased beyond a certain limiting value, usually about 0.1 ampere, the glow suddenly changes to an arc. In the arc discharge, the cathode current density is from a hundred to a thousand times that in the glow discharge, and the restricted spot from which the current issues may be very hot. It was for a time generally believed that high temperatures near, if not at, the cathode were essential for the maintenance of an arc.⁶

It has, however, been shown that the mercury-vapor arc can be operated with the cathode maintained at -70°C . or lower, the voltage being not much higher than in normal operation of the arc.⁷ Apparently exceptions to general rules are so frequent and the number of borderline cases so great that rigid definitions of the forms of gaseous discharge are scarcely attainable. The following were suggested by Thomson:⁸

Glow. A discharge between cold electrodes, the current being carried entirely by gaseous ions and electrons.

Arc. A discharge in which the current is carried by the material of the electrodes as well as by the gas between them.

Spark. The initial unstable stage in any discharge between cold electrodes

Spark and Arc Spectral Lines. The spectra produced by an arc and by a spark between similar electrodes may differ widely in character. An understanding of the origin of this difference, which is fundamental both historically and theoretically in the origin of atomic spectra, is essential to the employment of these sources in spectrographic methods for detection of the elements. Lockyer, a pioneer in solar spectroscopy, discovered that the intensities of certain lines occurring in the arc spectra of many elements are enhanced in their spark spectra.⁹ In some cases, lines occurring in the arc spectrum are missing in the spark spectrum; on the other hand, the spark spectrum may show lines not present in the arc spectrum. Lockyer demonstrated the appearance of new or "enhanced" lines in the spectra of stars, particularly in the Novae, and believed that they indicated the existence of hitherto unknown elements capable of existing only at the enormous temperatures of the stars, or under the conditions of temperature found in the spark. It has since been shown that "spark" lines can also be produced by the high temperature excitation of certain elements in a resistance furnace.

The key to the nature of these assumed new elements was given in Bohr's earliest paper on the theory of atomic structure. In 1897, Pickering had discovered in the spectrum of a certain star, besides the Balmer lines of hydrogen, a series of new lines, each of which lay about midway between two lines of the Balmer series. Their frequencies could be represented by the Balmer formula if for 3, 4, etc. in the second term, there were substituted 3.5, 4.5, etc. As he believed

⁶ For discussion, see Slepian, J., *J. Frank Inst.*, **1926**, 79; *Phys. Rev.*, **27**, 407 (1926)

⁷ Kawa, J., *Acta Phys. Polonica*, **1**, 427 (1932); Newman, F. H., *Phil. Mag.*, **18**, 607 (1934)

⁸ Thomson, J., *Phil. Mag.*, **13**, 824 (1932); see also McKeown, S. S., *Phys. Rev.*, **34**, 611 (1929) and Kaiser, H., and Wallraff, *Z. Physik*, **112**, 215 (1939) for transitions between the forms of discharge.

⁹ Lockyer, Sir Norman, *Proc. Roy. Soc.*, **30**, 22 (1879)

the new lines to be due to hydrogen, Pickering altered the Balmer formula to include them by making the Rydberg constant four times its usual value. The new lines were not, however, encountered in spectra excited in the laboratory until Fowler in 1912 observed them in the spectrum of a discharge tube containing both hydrogen and helium. Bohr realized that if a helium atom should lose an electron the resulting ion would resemble the hydrogen atom, except for the fact that its nucleus would bear two positive charges rather than one. He appreciated the necessity of incorporating the number of nuclear charges, *i.e.*, the atomic number, in his equation for the calculation of the energy associated with the rotation of an electron in an orbit, the expression which in his theory yields the Rydberg constant. As this expression involves the square of the nuclear charge, the result yields a constant four times as great when there are two nuclear charges as when there is but one. The constant for the helium spectrum would, therefore, be four times that for the hydrogen atom. This led Bohr to suggest that the Pickering lines are emitted by helium ions rather than by hydrogen, an explanation which met with much opposition until it was found that the lines could be observed in pure helium when suitably excited.

It is more difficult to excite helium to emit the Pickering lines than it is to cause this element to emit the ordinary lines observed in the glow discharge. In order to form the ion and induce it to emit energy, spark excitation is used. In general, spectra of the ions of elements are commonly called spark spectra, as distinguished from the arc spectra from the atoms of the same elements. These designations must not be taken too literally, since the so-called "spark" spectra of many elements may be produced by other means of excitation. Some lines of a spark series frequently appear in arc spectra, although they may be enhanced in intensity in the spark spectra of the same elements.

It has been noted that the spark spectrum of helium resembles the arc spectrum of hydrogen, the preceding element of the periodic table, the only difference being that the Rydberg formula must be altered to take account of the extra nuclear charge. Similar relations hold throughout the periodic system. The alkaline earth elements have two electrons in the outer ring. Loss of one of these on ionization causes the atom to resemble that of the preceding alkali metal and to give a spectrum like it when the excess nuclear charge is taken into account. The multiplicities of the ions of elements are closely related to those of the atoms of the preceding elements of the periodic table.

It is also possible to observe under suitable conditions spectra from doubly charged ions, or atoms which have lost two electrons. In some instances, still higher degrees of ionization have been studied. To distinguish between these spectra, Roman numerals are employed after the symbol of the element. Thus, C I refers to the spectrum of the neutral carbon atom, C II to that of the ion C^+ , C III to that of the doubly charged ion C^{++} and C IV to that of triply ionized carbon, C^{+++} . These are spectra of various orders, C I being of the first order. A given element excited by various methods produces different spectra, in each of which lines corresponding to one or another of these stages of ionization predominate. The demarcations are not sharp and it is common to find faint lines representing a higher degree of ionization superposed upon a spectrum of lines representing a lower stage of ionization. Antimony excited by a vacuum spark yields predominantly lines due to the doubly ionized atom Sb III. Tin in a Paschen hollow cathode in a discharge tube emits the lines of Sn II.¹⁰

¹⁰ Lang, R. J., *Phys. Rev.*, 35, 445 (1930).

In the atmosphere of the sun most of the elements are in the atomic state and yield the arc spectra. Spark lines are, however, observed in the case of a few easily ionized elements such as calcium. In the spectra of some stars, lines are found indicative of the presence of singly, doubly or further ionized ions. The appearance of lines of this character serves as a scale by which such bodies may be classified according to their temperatures. In the interiors of some of the stars, the temperatures reach millions of degrees and completely stripped atoms—mere nuclei—are believed to exist.

OTHER SOURCES OF ULTRAVIOLET RAYS OF LESSER IMPORTANCE

Incandescent Solids. The Nernst glower is said to yield a faint spectrum even beyond 2500Å. Not for many years, however, has it been employed as a source of ultraviolet rays.¹¹

Since about 1920, the incandescent tungsten lamp, operated at an abnormally high filament temperature, has been employed occasionally as a source of continuous ultraviolet rays for absorption studies. Lamps intended for this purpose, and provided with special quartz bulbs or windows, were described by Gehlhoff,¹² Franck and Grottrian,¹³ and by Stockbarger.¹⁴ Also, Stockbarger, Dingee and Burns¹⁵ have presented spectrograms showing that automobile headlight bulbs operated at a filament temperature of 3400°K. (at which they last but a few hours), permit the detection of radiations less than 3000Å when the bulbs are of lead glass. With soda-lime glass bulbs, emission to 2900Å could be detected, and measurements indicated that 0.046 per cent of the energy emitted through such bulbs lies below 3170Å. As this was over three times the amount of radiation expected in this region from the laws of black-body radiation, they concluded that there is a selective ultraviolet emission.

Luckiesh¹⁶ presented calculations of the percentages of the total emission which lie between 2800 and 3200Å from tungsten filament lamps of various wattages at several temperatures. His results indicated that such lamps would not be very effective sources for supplying this band of radiations to children. For the same total energies a quartz mercury arc gives 175 times as great an output in this region as does a tungsten filament lamp. Later calculations by Forsythe and Christison¹⁷ were more favorable. By utilizing data of Hulburt¹⁸ on the percentages of the total emissivity at 3400, 3800 and at 4200Å at various temperatures up to 2800°K. and employing certain considerations relating to the color temperature of tungsten, Forsythe and Christison obtained a curve for the spectral emissivity of tungsten at 2800°K. from the infrared to 2700Å. By a step-by-step integration, they secured from this curve values for the relative amounts of energy in various portions of the spectrum. From these values (at several temperatures) and the total wattages of the lamps were calculated theoretical amounts of energy in these spectral regions falling upon a square centimeter of surface at a distance of one meter from the filament. The absence of any absorbing bulb surrounding the filament was assumed. It was found that a 500-watt tungsten lamp burning

¹¹ Coblentz, W. W., *Bur. Standards Bull.*, **9**, 103 (1913); Griffiths, H. D., *Phil. Mag.*, **50**, 263 (1925).

¹² Gehlhoff, G., *Z. tech. Physik*, **1**, 224 (1920).

¹³ Franck, J., and Grottrian, W., *Z. tech. Physik*, **3**, 195 (1922).

¹⁴ Stockbarger, D. C., *J. Opt. Soc. Am.*, **9**, 337 (1924).

¹⁵ Stockbarger, D. C., Dingee, A. L., and Burns, L., *J. Opt. Soc. Am.*, **18**, 53 (1929).

¹⁶ Luckiesh, M., *J. Frank. Inst.*, **206**, 60 (1928).

¹⁷ Forsythe, W. E., and Christison, F., *General Electric Rev.*, **32**, 662 (1929).

¹⁸ Hulburt, E. O., *Astrophys. J.*, **45**, 149 (1917).

under conditions giving a life of 1000 hours would yield a total energy of 4 milliwatts per square centimeter, of which 0.0013 milliwatt was of wave-lengths shorter than 3250A and 0.00044 milliwatt was between 3100 and 2900 A. When the lamp was burned under 100-hour life conditions, the values were, respectively, 4.00, 0.0017 and 0.00060. A 900-watt motion-picture lamp gave 9.2, 0.0076 and 0.0028 milliwatts. These values compared favorably with the energy of the sunlight passing through an air-mass of 2.37 atmospheres, which gave 0.010 milliwatt of energy shorter than 3250A and only 0.00017 between 3100 and 2900A. The total energy of the sunlight was, however, far greater, 33.9 milliwatts.¹⁹

Borstler²⁰ proposed the therapeutic use, by means of a quartz applicator, of ultraviolet radiations from a 6- or 8-volt tungsten automobile headlight in a Pyrex bulb, operated at voltages 10 per cent above normal.

Flames. As sources of ultraviolet radiations, flames are of little value. They are employed occasionally in conjunction with sparks in certain methods of quantitative analysis by spectrographic methods. In the early work in the visible region, flames were used as a ready means of vaporizing salts and exciting the metallic portions thereof, particularly the alkalis, which readily give characteristic lines.²¹ To make the method available for the detection of elements more difficult to excite, higher temperatures are necessary. Early students of line spectra²² secured these by directing an oxyhydrogen blowpipe upon the solid to be examined. Still higher temperatures may be attained with the aid of the oxyacetylene flame.²³ The spectrum produced in the flame itself is sometimes a complicating factor. It is a band spectrum emitted by the molecules of water vapor produced during combustion. The lines of these bands are weak at wave-lengths greater than 3200A and interfere but little with analyses based upon lines situated at longer wave-lengths.

Before the development of the mercury arc or the appreciation of the value of other simpler arcs, flames were occasionally employed as sources in the study of reactions produced by ultraviolet rays. Wulf employed a flame of carbon disulfide and oxygen for such purposes.²⁴

Bombardment by α -rays²⁵ or cathode-rays²⁶ has been used in investigations in the region of wave-lengths longer than those of the usual x-rays.

Among the less important electrical sources of ultraviolet radiation is the exploded wire method of Anderson²⁷ although it has occasionally been of service in the study of the absorption spectra of vapors. In this method, a fine wire (less than 36-gauge), 5 cm. in length, of nickel, iron, manganese or copper, is fused or exploded by discharging through it a heavy current by means of a large condenser charged by a 500-watt, 26,000-volt transformer, suitably rectified. In series with the wire is an adjustable spark-gap. In air, the method yields a nearly continuous spectrum, with many dark lines, due to absorption by the hot metal vapor.

¹⁹ For other data on the emission of tungsten filaments, see von Alphen, H. C., *Ann. Physik*, **85**, 1058 (1928) and Hoffmann, F., and Willenberg, H., *Physik. Z.*, **35**, 713 (1934).

²⁰ Borstler, E. W., U. S. P. 1,800,277, April 14, 1931.

²¹ For a general discussion, see Lohse, H. W., *Can. J. Research*, **12**, 519 (1935), and Lundegård, H., *Lantbruks-Högskol Ann.*, **3**, 49 (1936).

²² Lockyer, Sir N., and Austen, R., *Proc. Roy. Soc.*, **23**, 344 (1875); Liveing, G. D., and Dewar, J., *ibid.*, **28**, 352 (1879); Hartley, W. N., *Phil. Trans.*, **185A**, 161, 1047 (1894).

²³ Hemsalech, G. A., and de Wetteville, C., *Compt. rend.*, **149**, 1112, 1369 (1909); de Gramont, A., *ibid.*, **157**, 477 (1918); **176**, 1104 (1923).

²⁴ Wulf, T., *Ann. Physik*, **9**, 946 (1902).

²⁵ Greinacher, H., *Z. Physik*, **47**, 344 (1928).

²⁶ Collin, W. M., *Z. Physik*, **70**, 662, 667, 679 (1931).

²⁷ Anderson, J. A., *Astrophys. J.*, **51**, 37 (1920).

In place of wires, asbestos fibers may be used upon which solutions of the various alkaline-earth chlorides to be analyzed have been evaporated.²⁸

A very brilliant light (up to 14,000,000 candles) of extremely short duration (less than 5 millionths of a second) is said to be produced by the explosion in argon of 0.4 cc. of a liquid explosive, such as tetranitromethane. Its spectrum extends far into the ultraviolet.²⁹

Electrodeless Discharge. The high-frequency electrodeless discharge has been but rarely employed for carrying out photochemical reactions. Since its discovery by Hittorf in 1884, there has been much discussion as to whether the phenomenon is to be ascribed to an electrostatic or an electromagnetic field.³⁰

Apparently either can excite a gas or vapor at low pressure to emit a brilliant diffuse discharge. In these methods, the oscillatory discharge from a condenser goes through a coil of wire surrounding but not touching the reaction vessel. At higher gas pressures, the discharge alters in character and assumes a ring form, the lines changing from a mixture of arc and spark lines to a spectrum in which spark lines predominate. Harkins³¹ used a coil of six turns of copper wire around a quartz or "Pyrex" flask with a side-tube arranged for the collection of the products formed during the passage of the discharge through various organic gases. A window was arranged for spectrographic observations of the products transiently produced. The frequency of the circuit was 800 kilocycles per second. The circuit included a 1 k.v.a. Thordardsen transformer which supplied a maximum of 25 kilovolts, a spark gap of cylindrical zinc electrodes adjustable by a screw, and a 0.025 microfarad condenser. In the discharge, both benzene and acetylene were found to be dissociated, giving spectrographic evidence of the presence of H, C, C⁺, C₂ and CH. Polymerization led to compounds of very high molecular weights which appeared as solid, reddish brown flakes. At a pressure of 0.02 mm., 5000 liters of benzene vapor were passed into the flask without changing the character of the discharge; from one to two grams of solid products were formed per hour.

Another type of apparatus³² is that in which rare gases, especially krypton and xenon, in a vessel at low pressure are subjected to an electric current or electromagnetic field of high intensity by a high frequency coil. It has a quartz window for ultraviolet irradiation processes so disposed as to be practically outside the high-frequency field. The rare gases emit a gamut of rays from the visible to the very short ultraviolet of value in therapy. The surrounding solenoid is placed far enough from the window so that the latter does not become very hot, permitting the application of the source very close to the part of the body to be irradiated. This lessens the loss of short ultraviolet rays by absorption by the air. The ends of the solenoid wire are joined to a high-frequency apparatus, such as a spark-gap diathermy apparatus. In the discharge in neon, the current density is important, as neon at high current densities emits intensely between 3350 and 3700 Å.³³ At current densities greater than three amperes per square centimeter, the source emits a spark spectrum, high frequency not being required.

²⁸ Sawyer, R. A., and Becker, A. L., *Astrophys. J.*, **57**, 98 (1923)

²⁹ Michel-Lévy, A., and Maurarour, H., *Compt. rend.*, **200**, 543 (1935)

³⁰ Stuhlman, O., Jr., and Whitaker, M. D., *Rev. Sci. Instruments*, **1**, 772 (1930); Rayleigh, Lord, *Proc. Roy. Soc.*, **150A**, 34 (1935). For the construction of light sources of this sort in the laboratory, see Winans, J. G., *Rev. Sci. Instruments*, **9**, 203 (1938)

³¹ Harkins, W. D., *Trans. Faraday Soc.*, **30**, 221 (1934)

³² French P. 743,167, *Match* 25, 1933, to Soc. anon. pour les Applications des Gaz Rares à la lumière, procédé, George Claude; British P. 385,835, Jan. 5, 1933; *Brit. Chem. Abs.*, **B**, 1933, 197, *Chem. Abs.*, **27**, 3671 (1933). Goude-Axelos, J., and Claude, A., *Compt. rend.*, **194**, 132 (1932).

³³ Soc. anon. pour les Applications des Gaz Rares établissements Claude-Paz and Silva, British P. 404,271, Jan. 8, 1934

The sparking potential in electrodeless discharge tubes diminishes when the tube is illuminated by ultraviolet or visible light ³⁴

Radiations produced in metal vapors by the passage of radiations from another source or those furnished by active nitrogen or hydrogen, although theoretically important, do not at present constitute practical sources of ultraviolet radiations.

³⁴ Zouckermann, R., *Compt rend.*, **206**, 331 (1938).

Chapter 4

The Spark as a Source of Ultraviolet

The electric spark is rather infrequently used as a source of ultraviolet radiations for effecting photochemical reactions, although it has been employed in some of the more important investigations. The electric spark finds its chief application as a source of a many-lined spectrum suitable for studying absorption spectra of compounds possessing broad absorption bands. (See also Chapter 9.) It is also widely employed as a means of exciting to emission materials to be analyzed by spectrographic methods. Sparks passed in vacuum have yielded information of importance in the region of the extreme ultraviolet. The high tension disruptive electric spark between iron terminals is very rich in ultraviolet radiation and is useful in producing fluorescent effects, particularly in mineral and drug analyses. It is, however, seldom used for this purpose.

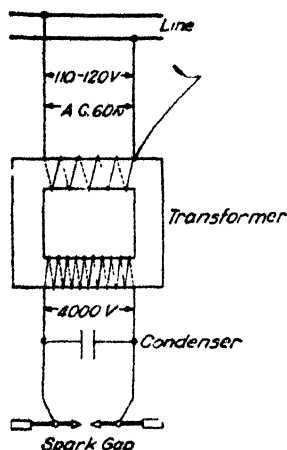


FIGURE 5.
Diagram of Connection, Iron
Spark Apparatus

(Courtesy General Electric Co.)

Iron electrodes were used in a spark outfit designed by Andrews.¹ The connections of the apparatus are shown in Figure 5. A small transformer steps up a 60-cycle, 110-120 volt, alternating current to about 4000 volts. A condenser is connected in series with the iron terminals. The spark gap is adjustable. Assembled apparatus is shown in Figures 6 and 7. As this apparatus uses only about 250 to 300 watts, it can be safely connected to any alternating current lighting circuit.

Ross² recommended the use of aluminum terminals, which yielded an intensity of ultraviolet radiation (measured by the liberation of iodine from potassium iodide) twice as great as that resulting when terminals of any other common

¹ Andrews, W. S., *General Electric Rev.*, April, 1916, 319.

² Ross, W. H., *J. Am. Chem. Soc.*, 18, 786 (1906).

metals were used. Cadmium was not recommended because of its softness. The terminals were 3 mm. \times 8 mm. in cross-section and were placed 7 cm. apart on iron plates. Small dishes, containing ice and resting on the metal, served to conduct away the heat rapidly.

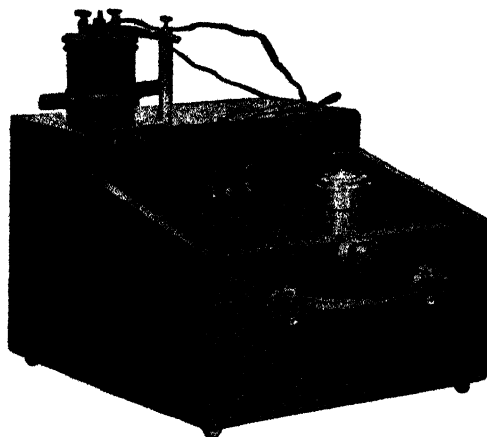


FIGURE 6.

Rear View of "Iron Spark"
Apparatus.

(Courtesy General Electric Co.)

ELECTRICAL CIRCUITS EMPLOYED FOR THE PRODUCTION OF SPARKS

When a small potential difference is impressed upon two parallel electrodes separated by an air space, a very small current will be carried across the gap by the few ions present in the air as a result of cosmic rays, radioactivity, etc. As the potential difference is increased, the current increases in accordance with Ohm's law but only so long as the potential difference remains small. With further increases, the current increases less and less rapidly and finally becomes constant (saturation value) over a wide range of impressed potential differences.

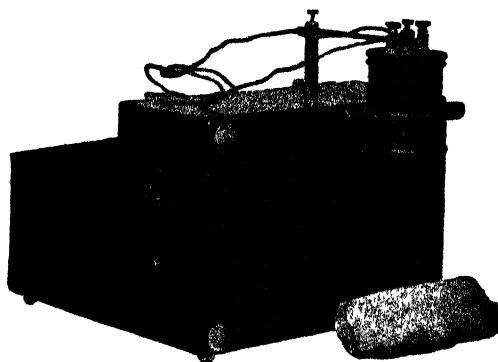


FIGURE 7.

Front View, Portable "Iron
Spark" Apparatus.

(Courtesy General Electric Co.)

This occurs because the electrons in a dense gas collide with gas molecules before the electrons can acquire sufficient kinetic energy (from the potential field) to ionize the gas. Thus no new carriers of current are produced.

When the potential difference has been raised to several thousands of volts,

ionization by electron impact occurs suddenly and the current rapidly attains high values. There is a brilliant flash, a spark passes across the gap with the production of a high temperature and the potential difference is temporarily obliterated.

The spark is very brief in duration. What happens following it depends on the nature of the external circuit. Under suitable conditions, the air becomes ionized, the resistance drops, and some form of self-maintained discharge ensues. This may take the form of an arc if the heat of the spark has brought the electrodes to a sufficient temperature. To produce sparks across small gaps, gradients of about 30,000 volts per centimeter are required.³ The earliest workers to study spark spectra⁴ used an induction coil to produce the necessary high potentials. By photographic methods, with rapidly moving films, Schuster and Hemsalech⁵ showed that the emission of metal lines was due to an oscillating discharge, and that, following a single discharge through the air, which vaporizes the electrode material, the lines form near the electrodes and then cross the gap at rates of 400 to 1300 meters per second. The particles composing the streamers were found to be electrically charged.⁶

Studies with rotating mirrors have shown that a break in the primary circuit of the induction coil causes a series of secondary discharges, the first of these secondary discharges being bright and the others faint. The first is a true spark, since it may be shown (by the oscillograph) to follow upon a very high potential difference between the terminals of the secondary winding. Such a discharge, repeated at each interruption of the primary current, emits a spectrum which is characteristic of the gas through which it passes, and exhibits but a few faint lines from the metal of the electrodes. Early spectroscopists spoke of this spark as "uncondensed," a term now known to be incorrect, since all sparks are associated with a condenser discharge. In this case the condenser was the air-gap itself together with the capacity of the secondary winding. In all sparks, the discharge is oscillatory because of the inertia effect of self-induction in the winding. Most workers, however, employed a condenser (in parallel with the spark gap) charged by the induction coil to the necessary sparking potential. (Figure 5.)

The induction coil may be replaced by a small high tension alternating current transformer, thus eliminating difficulties arising in the operation of contact-breakers. As in the case of the induction coil, the capacity of the condenser determines the quantity of electricity which passes in each spark and the intensity of the spark. Only when the condenser capacity is sufficient is the discharge strong enough to vaporize the electrode material into the discharge, there to emit its characteristic lines. With condensers of high capacities, the intensity is sufficient to ionize the atoms of the electrode metal and produce the spark spectrum of the latter. The sizes of transformer and condenser must be so chosen that the sparking potential may be obtained or exceeded. Details of transformer and condenser requirements are found in a paper by Anderson⁷ and in the publications of the makers of spectrographic equipment.

³ For further detailed discussions of spark theory, see Loeb, L. B., *Rev. Modern Phys.*, **8**, 267 (1936); Rogoski, W., *Z. Physik*, **100**, 1 (1936); Pirani, M., *Angew. Chem.*, **44**, 395 (1931); Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932.

⁴ Hartley, W. N., *Phil. Trans. Roy. Soc.*, **1**, 50 (1884); **II**, 327; Pollok, J. H., and Leonard, A. G., *Proc. Roy. Soc. Dublin*, **11**, No. 16, 17, 18 (1907); No. 23, 24 (1908), No. 31 (1909).

⁵ Schuster, A., and Hemsalech, J. G., *Phil. Trans.*, **193A**, 189 (1900).

⁶ Milner, S. R., *Phil. Trans.*, **209**, 71, 1908, see also Royds, T., *Ibid.*, **208**, 333 (1908); *Phil. Mag.*, **19**, 285 (1910). Their velocities have been measured recently. Miyazishi, M., *Japan. J. Phys.*, **5**, 67 (1928); *Chem. Abs.*, **23**, 4404 (1929). Asami, Y., *Elec. Eng. Japan*, **53**, 27 (1933); *Chem. Abs.*, **27**, 2630 (1933). Toriyama, Y., and Shinohara, U., *Elec. Eng. Japan*, **53**, 100 (1933); *Chem. Abs.*, **27**, 2630 (1933).

⁷ Anderson, J. A., *Astrophys. J.*, **59**, 76 (1924).

A high capacity condenser causes slower oscillations in the discharge, thereby increasing the amount of electricity secured in each oscillation. This prolongs the train of sparks and produces a heating effect on the electrodes. de Kowalsky⁸ showed that the region of maximum radiated energy is displaced toward the longer wave-lengths as the oscillatory current is increased. Increasing the amount of energy consumed in the spark, however, causes displacement in the opposite direction, although this is to some extent dependent upon the nature of the electrodes. The intensity of the mean ultraviolet radiation emitted varies inversely with the frequency.

The oscillations may also be made slower by introducing additional self-inductance, the rate of oscillation varying inversely as the square root of both the capacity and self-inductance of the circuit. A self-inductance coil, called frequently a Hemsalech coil,⁹ has the property of making the "air-lines" disappear, the spectrum being then largely from the electrodes. The self-inductance coil is introduced in series with the gap at A in Figure 8.

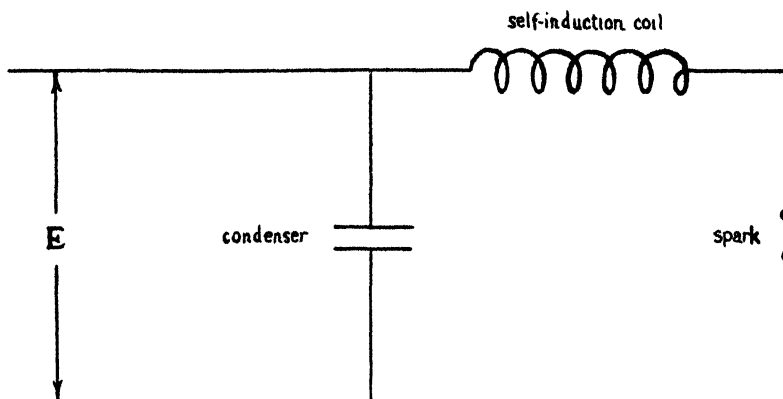


FIGURE 8 Diagram of Spark Circuit. (Twyman and Smith, "Wavelength Tables for Spectrum Analysis" London, Adam Hilger Ltd.).

The form of the discharge depends upon the amount of self-inductance employed since the latter decreases the rate of oscillations, and also lessens the current which passes in the first discharge, spreading the current more evenly over a series of oscillations. Without any self induction, the oscillations are strongly damped by the resistance of the gap, so that most of the energy passes in the first spark. With self-induction, less current passes during the first spark and the oscillations continue for a longer time.

In the first case (no self-induction), the first strong spark is believed to excite the gas and to send some vaporized metal from the electrodes. The discharge then dies away rapidly and the metal vapor cools. Subsequent oscillations are too weak to vaporize more metal. With but little metal vapor in the gap, the resistance and potential are high and the electrons acquire sufficient kinetic energy to excite the gas. With self-inductance the first spark is not strong enough to excite the gas and its lines are not evident. The cumulative effect of the subsequent discharges is, however, sufficient to heat and vaporize the metal. The introduction of this

⁸ de Kowalsky, I., *Compt. rend.*, **158**, 1337 (1914); *Bull. Soc. Int. Elect.*, **4**, 437

⁹ Hemsalech, T. A., *Compt. rend.*, **122**, 285 (1899); Schenck, C. C., *Astrophys. J.*, **14**, 436 (1901); *Phil. Trans.*, **193A**, 189 (1900).

GOVERNMENT OF
13924

heated metal vapor into the gap lowers the resistance and the potential and the electrons fail to acquire sufficient energy to excite the gas. As the metal becomes ionized when the spark carries enough current, all of the arc lines are present. The prolongation of the oscillations under these conditions led de Gramont to speak of such sparks as oscillating sparks as distinguished from the condition which he called the "condensed" spark. This is misleading for both are oscillatory and condensed in fact.¹⁰

The effects of variations in capacity and self-inductance are particularly important when the spark is employed as a source for the spectrographic analysis of metals. Since spectrographic analysis involves technique which requires considerable experience and since this subject does not fall within the province of this book, further details must be sought in manuals devoted to spectrographic essays. For spectrographic analysis, Scheibe and Neuhausser recommended¹¹ 0.0033 mfd. capacity and 0.000015 henry of self-induction. Resonance transformers¹² and high frequency transformers have been recommended.¹³

"Hot Sparks." By employing large induction coils together with condensers of high capacity, it is possible to obtain spectra representative of high degrees of ionization. So-called "hot sparks" with very narrow gaps were employed by Millikan¹⁴ in his work on the short wave-length spectra of stripped atoms. As the sparking was done in a vacuum, air-lines were not a disturbing feature, so that low self-inductance could be used. The intensity was controlled by an adjustable auxiliary spark-gap in series with the spark to be studied. The operation of these sparks has been described by Sawyer.¹⁵ Robinson¹⁶ estimates that temperatures of 300,000°K. can be attained by such methods. Edlén¹⁷ in studying the C V spectrum at wave-lengths as short as 40.28Å, employed a vacuum spark with a capacity of 0.3 μ F, charged to 60,000 volts. With thirty sparks passing per minute, and a metal grating employed at a glancing angle of 5.4°, he found half an hour sufficient for an exposure.

THE ARRANGEMENT OF THE ELECTRODES OF SPARK SOURCES

In studying the emission spectra of metals or alloys, it is necessary to support two blunt-pointed rods or heavy wires of the material so that a gap is formed. Adjustable supports for the rods are desirable. The spectra of minerals can be obtained by attaching them to rods by spring clips.¹⁸

Boas¹⁹ passes a high speed current of air past the spark in order to destroy the aureole surrounding it. He also describes an electrostatic relay to maintain a constant distance between the electrodes. The latter erode rapidly if thin. On

¹⁰ See also Negresco, T., *J. Chim. Phys.*, **25**, 308 (1928).

¹¹ Scheibe, G., and Neuhausser, A., *Angew. Chem.*, 1218 (1928), see also Meggers, W. F., Kiess, C. C., and Stimson, F. J., *Bureau of Standards Sci. Paper No. 444*, 1922; Sweitzer, E., *Z. anorg. allgem. Chem.*, **164**, 127 (1927); Kosbahr, T., *Ann. Physik*, **25**, 625 (1936); Gibbs, R. C., Vieweg, A., and Gaertlein, C. W., *Phys. Rev.*, **34**, 406 (1929); Langstroth, G. O., and McRae, D. R., *Canadian J. Research*, **16A**, 17, 61 (1938).

¹² Boas, H., *Z. Physik*, **60**, 690 (1930).

¹³ Hull, F. A., and Steele, G. J., *Proc. Am. Soc. Testing Materials*, **27**, II (1927); Gerlach, W., and Schweitzer, E., *Z. anorg. allgem. Chem.*, **195**, 255 (1931); Potopenko, G., *Ibid.*, **215**, 44 (1933); Goroncy and Urban, *Ibid.*, **211**, 28 (1933); Feussner, O., *Z. Metallkunde*, **25**, 73 (1933).

¹⁴ Millikan, R. A., *Astrophys. J.*, **52**, 47 (1921); **53**, 150 (1921); *Phys. Rev.*, **12**, 168 (1918); *Science*, **19**, 138 (1919).

¹⁵ Sawyer, R. A., *Astrophys. J.*, **52**, 286 (1920); Sawyer, R. A., and Smith, F. R., *J. Opt. Soc. Am.*, **14**, 287 (1927).

¹⁶ Robinson, H. A., *Z. Physik*, **100**, 636 (1936).

¹⁷ Edlén, B., *Nature*, **127**, 405 (1931).

¹⁸ Heraeus, W. C., G.m.b.H., *British P.* 400,607, Oct. 18, 1933.

¹⁹ Boas, H., *Z. Physik*, **60**, 690 (1930).

the other hand the spark may move from place to place on a thick electrode. Gring and Clark²⁰ described a stand capable of holding four pairs of electrodes, any pair of which can be quickly brought into position for exposure.

Arrangement of Electrodes. Spark sources have been employed in measuring the extent of some photochemical reactions. In such cases, uniformity over a prolonged time is necessary. Forbes and Brackett secure this by striking the spark²¹ between adjacent edges of two square bars of metal (see Figure 9). The latter

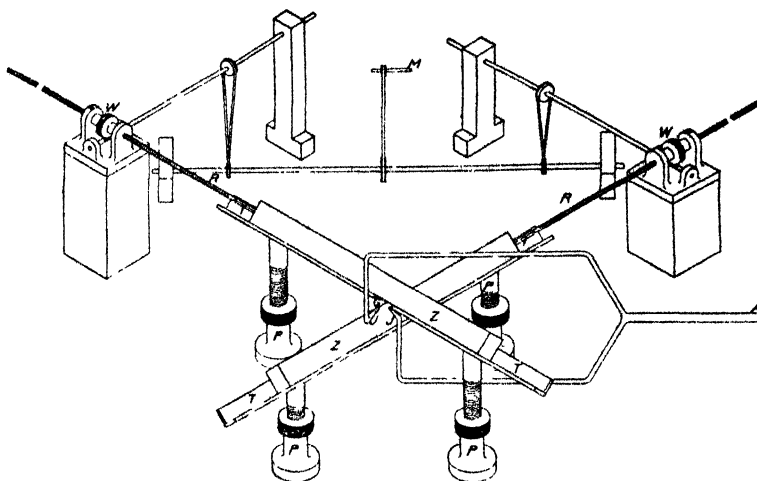


FIGURE 9. Spark Source for Automatically Constant Illumination (Forbes and Brackett, *Journal American Chemical Society*).

move in horizontal planes at right angles to each other. Conduction and radiation of heat are so rapid that erosion is at a minimum. The method avoids hand control required by previous workers with sparks and monochromators.²² In the apparatus, flexible woven metallic bands connect two $400 \times 25 \times 25$ mm. bars to a condenser. The bars rest in rectangular troughs perpendicular at right angles. Posts P are insulated from the base board by vulcanite blocks. The upper trough is cut away at G to expose the lower edge of the upper bar. The ends of the troughs are raised or lowered by turning the milled heads until the bars are horizontal, and their separation along the common diagonal is 2 mm. The shortest path for the spark lies along this one line. Blasts of air provided by two vacuum cleaners in tandem converge from the jets J upon the gap at G to blow back the corona. A ventilated housing conducts away oxide fumes. Threaded rods R, ending in insulating links I, pass through sleeves rotated by worm gears W, retracting the bars. The optimum speed varies with the energy of the spark and the volatility of the metal. Zinc bars, operated at 250 mm. per hour, give $1\frac{1}{2}$ hours net service for each of the four pairs of edges. When a pair of edges has been used up, the current is interrupted, the oxide crusts detached, the threaded rods

²⁰ Gring, J. L., and Clark, G. L., *Rev. Sci. Instruments*, **7**, 305 (1936).

²¹ Forbes, G. S., and Brackett, F. P., Jr., *J. Am. Chem. Soc.*, **53**, 3973 (1931).

²² Warburg, E., *Sitzb. Preuss. Akad. Wiss.*, 746 (1911); Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, **52**, 124 (1930).

returned to their original positions, and operation is started with a fresh pair of edges. The depth of erosion on the upper edge is constant at 1.2 mm. for zinc and 0.5 mm. for aluminum. On the lower edge, it is about two-thirds as much. A 5 kv. oil transformer is operated at 110 volts and 35 amperes under control of a voltage regulator. The gap voltage is 6500 ± 500 , secured by employing a heavy duty mica condenser of 0.04 microfarad capacity.

With the monochromator employed, it was possible to secure approximately monochromatic radiations in the case of zinc of 30,000 ergs per second at 2530Å, and of 16,000 at 2080Å. With cadmium, the intensities attained at the slit were 34,000 ergs per second at 2170, 79,000 at 2260, 22,000 at 2570 and 27,000 at 2710Å. The intensities attainable with aluminum electrodes were lower. Forbes²³ regarded the spark as an almost indispensable source of radiations of wave-lengths shorter than 2500Å. He noted that the zinc spark employed by Warburg in his early work gave²⁴ at 2540Å a thousand-fold the intensity of a mercury vapor lamp.

Lifschitz²⁵ obtained intense light and high temperatures by sparking between the whole length of a pair of electrodes. Ogg, Leighton and Bergstrom²⁶ describe a spark gap (Figure 10) in which the spark passed between the tapered edges of two rotating disks of cobalt or cadmium, A,A' mounted on hollow shafts, B,B', through which cooling water was circulated. To provide insulation, the cooling water circuit was broken by sprinklers. The frames holding the shafts were movable, so that the gap length, usually about 1 cm., could be adjusted by the screws I,I'.

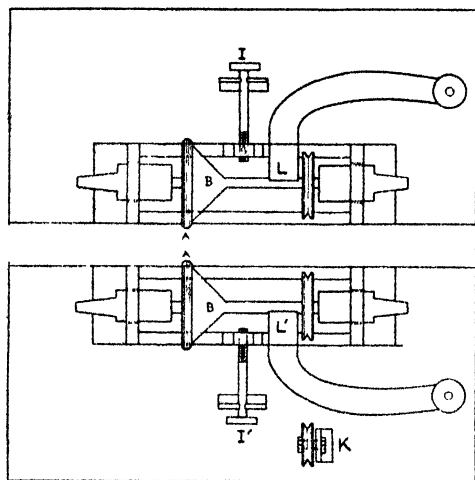


FIGURE 10.

Spark Gap with Rotating Water-cooled Electrodes (Ogg, Leighton and Bergstrom, *Journal American Chemical Society*).

The shafts were belt-driven in opposite directions at several hundred r.p.m. by a $\frac{1}{4}$ h.p. motor. Electrical contact was made through heavy carbon brushes L,L', connected to the terminals of a 0.010 mfd. oil-immersed condenser across the secondary of a 5 kw. x-ray transformer. By this means one to two discharges per half cycle were obtained across the gap. A hose (attached to a vacuum line)

²³ Forbes, G. S., *J. Phys. Chem.*, **32**, 485 (1928).

²⁴ Warburg, E., *Sitzb. Preuss. Akad. Wiss.*, 746 (1911), 216 (1912), 314 (1916).

²⁵ Lifschitz, S., German P. 524,877, March 26, 1926, *Chem. Abs.*, **25**, 4189 (1931).

²⁶ Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933). See also van der Lingen, J. S., *S. African J. Sci.*, **33**, 197 (1937).

mounted close behind the spark drew off objectionable fumes. The gap was readily demountable for cleaning and oiling of the bearing and interchange of electrode disks.²⁷

PHOTOCHEMICAL REACTIONS IN GASES SURROUNDING SPARKS

Jolibois, Lefebvre and Montagne²⁸ state, from observations on the change in pressure, that carbon dioxide at pressures between 0.3 and 20 mm. of mercury when subjected to a spark discharge, is decomposed into carbon monoxide and oxygen. A limiting dissociation of 90 per cent is attained. About 20 per cent of the energy of the first spark is converted into chemical energy; the remainder is dissipated. The decomposition increases with the voltage and is influenced by the size and shape of the containing vessel and the position of the electrodes. The yield rises to a maximum and falls as the capacity of the circuit decreases, and for a given capacity the maximum yield falls off slightly as the pressure increases.

Methane, under a pressure of 1 to 11 mm., was transformed into ethylene and hydrogen²⁹ under a spark discharge. Apparently little industrial use has been made of the radiations from a spark gap, although its use as a means of generating a bleaching gas for flour and cornmeal has been patented.³⁰

²⁷ For other spark apparatus, see Henri, V., *Compt. rend.*, **157**, 126 (1913); Kuhn, W., *Ibid.*, **178**, 708 (1924).

²⁸ Jolibois, P., Lefebvre, H., and Montagne, P., *Compt. rend.*, **182**, 1026 (1926), **184**, 522 (1927). General discussions are due to Lefebvre, H., *Chimie et Industrie*, Special Number, June, 427, 1933, and to Jolibois, P., *Ber.*, **71A**, 73 (1938).

²⁹ Montagne, P., *Compt. rend.*, **194**, 1490 (1932).

³⁰ Stiff, F., German P. 510,419, Dec. 23, 1927, *Chem. Abs.*, **25**, 1008 (1931), German P. 518,201, June 28, 1929, *Chem. Abs.*, **25**, 2377 (1931), German P. 521,360, Dec. 25, 1929; *Chem. Abs.*, **25**, 2651 (1931), Brabender, C. W., *Mehlprobleme*, **1**, 6 (1932).

Chapter 5

The Open Arc

Arcs may be produced between electrodes that are open to the air or enclosed in a vessel of glass or quartz. In the case of the enclosed arcs, the pressure may be very low or it may be atmospheric or greater.

In most arcs, the use of very high starting potentials is obviated by bringing the electrodes into contact (closed circuit) and then drawing them apart. The resistance offered to the passage of the current heats the electrodes to a temperature such that, when drawn apart, they produce vapors of the electrode material. The latter carry a bright discharge across the intervening space. The arc discharge, which may carry many amperes, is very hot and the electrodes become brightly luminous.

The mechanical features of the arc vary with the use for which it is intended, as commercial illumination, spectrographic analysis, as an ultraviolet source for conducting photochemical reactions or for fluorescence studies. An arc which will emit ultraviolet energy strongly may be prepared by employing an iron rod and a carbon rod for the two poles. Also, two iron rods may be used. These poles are cooled by means of heavy brass or copper sleeves, which may be moved along the iron rods as the latter are consumed. Thus, the upper pole (negative) may be an iron rod about one-quarter inch in diameter. This rod is surrounded by a movable but well-fitted sleeve of copper about one inch in diameter with hollowed end. One pole should be adjusted vertically. In preparing the arc, a bead of molten metal is developed in the dished end of the lower electrode. The upper electrode is well cooled and the arc is maintained very steadily between the bead of molten iron and the upper solid electrode. Luckiesh has had such an arc operate at a rather high current density for thirty minutes without any adjustment.

ELECTRICAL CHARACTERISTICS

Metallic arcs in general will not burn on alternating current. The carbon (but not the graphite) arc will, however, burn on alternating currents at potentials as low as 80 volts. On direct current, the carbon arc burns with voltages as low as 37. Iron and copper arcs require higher voltages, 80 and 90 at least. Arcs between electrodes of materials with good thermal conductivity tend to extinguish readily.

A number of observers have developed empirical equations for the relation between the length of the arc and the voltage, or between the energy, current, voltage and arc length.¹ The Ayrton equation for the carbon arc, $V = A + B/I$, has been made more accurate and more general by Nottingham by raising the current I to a power n . A and B are constants depending upon the arc length

¹ Ayrton, Mrs. H., "The Electric Arc," Chapter IV, New York, van Nostrand, 1902; Malcolm, H. W., and Simon, H. T., *Physik. Z.*, 8, 471 (1907); Steinmetz, C. P., *Trans. Am. Inst. Elec. Eng.*, 802 (1906); Bramhall, E. H., *Phil. Mag.*, 13, 682 (1932); Nottingham, W. B., *Am. Inst. Elec. Eng.*, 42, 12 (1923); *Phys. Rev.*, 28, 764 (1926); Anderson, S. H., and Kretschmar, G. A., *Phys. Rev.*, 26, 33 (1925); Doan, G. F., and Myer, J. L., *Elec. Eng.*, Sept., 1932; Sommer, J. J., and Bott, J., *Physik. Z.*, 34, 324 (1933); Kotecki, A., *Acta Phys. Polon.*, 4, 113 (1935).

and pressure. The equation applies if the anode is very hot. The power n is a constant dependent upon the boiling or sublimation point of the metal of the anode. It is 0.67 for copper, 1.38 for tungsten, and approximately 1 for carbon, the latter accounting for the success of the Ayrton equation. The dependence of this constant upon the nature of the anode led Myer² to suggest that the anode may have a more important role in the arc mechanism than most theories of the arc discharge would imply. Alterthum and Ewest³ believe that the anode exerts an important effect over the entire discharge, for by preheating the anode, the striking and operating voltage of the arc can be greatly reduced. Hagenbach and Langbein⁴ stated that in normal arcs, the anode is boiling during discharge. The form of the equation also shows that an increase in the current is accompanied by a drop in the potential, showing that Ohm's law does not apply to conduction in the arc.

With heavy currents, above ten amperes, the voltage approaches the limiting value A . The pressure of the gas is also a factor. The required potential increases continuously with the pressure; the values at ten atmospheres may be 15 to 20 volts greater than at one atmosphere.⁵

The theory of the mechanism of the arc discharge has lagged somewhat behind practice. The development of the quartz mercury-vapor arc was based to a large extent upon empirical observations and trial and error methods. The theory of the open arc is still the subject of many controversial statements.⁶ The development of arc theory may be approached through a consideration of the phenomena of glow discharge at low pressures, which has been summarized by Dushman,⁷ Langmuir,⁸ and by Pirani.⁹

The various easily recognizable regions of the glow discharge are also found in arcs through gases at low pressures but are masked in the high-pressure or open arc. The theories of the latter are, however, based upon the application of principles derived from the study of the glow discharge. The fundamental processes of the emission of electrons from hot cathodes, the liberation of electrons by thermal ionization of atoms and molecules of gases, the acceleration of electrons in potential fields and the results of impact of electrons with atoms and molecules leading to excitation and the emission of radiations, all are encountered in high-pressure or open arcs as they are in the glow discharge. Complications in study of open arcs arise from such effects as the high temperature glow of the electrodes, vaporization and sputtering of the electrodes and combustion in the flame of the arc.

Thermionic emission of electrons from the cathode, heated by positive ion bombardment, has been believed adequate to account for the current densities in the tungsten arc or carbon arc.¹⁰ Although the temperatures of the copper, iron and

² Myer, J. L., *Trans. Am. Inst. Elec. Eng.*, **52**, 250 (1933).

³ Alterthum, H., and Ewest, H., *Z. tech. Physik*, **9**, 221 (1928).

⁴ Hagenbach, A., and Langbein, K., *Arch. Sci.*, **1**, 48 (1919).

⁵ See also Anderson, S. H., *Phys. Rev.*, **29**, 750 (1927).

⁶ For a detailed earlier account, see Compton, K. T., *J. Am. Inst. Elec. Eng.*, **46**, 868, 1192 (1927).

⁷ Dushman, S., *Elec. Eng.*, **53**, 1204, 1283 (1934).

⁸ Langmuir, I., *Gen. Electric Rev.*, **38**, 514 (1935).

⁹ Pirani, M., *Z. angew. Chem.*, **44**, 395 (1931); Lex, E., Pirani, M., and Rompe, R., *Naturwiss.*, **23**, 393 (1935). See also for greater details, Langmuir, I., and Compton, K. T., *Rev. Mod. Physics*, **3**, 191 (1931); Found, C. G., and Forney, J. D., *J. Am. Inst. Elec. Eng.*, **47**, 747, 855 (1928); Kirschstein, B., and Koppelman, F., *Z. tech. Physik*, **15**, 604 (1934), and the books, Kohler, W., and Rompe, R., "Die Elektrischen Leuchtöhre," Vieweg, 1933; Seeliger, R., "Physik der Gasentladungen," Leipzig, Barth, 1927; Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932.

¹⁰ Nottingham, W. B., *J. Frank. Inst.*, **205**, 811 (1928); Mason, R. C., *Phys. Rev.*, **38**, 427 (1931).

nickel arc cathodes have been found to lie near the boiling points of these metals¹¹ such temperatures are said to be too low to produce sufficient electrons to give the observed current densities.¹² Furthermore, so-called "cold cathode" arcs are known to be obtainable.¹³ Slepian reported that the arc current to the cathode may be carried by positive ions resulting from thermal ionization of the gas, in accordance with the Saha equation. The necessary temperatures of 6000 to 7000° were assumed to exist in a thin layer of gas next to the cathode. Langmuir¹⁴ introduced a different theory in which electrons are assumed to be drawn from the cathode by a very intense electrostatic field near the cathode surface set up by a positive space-charge sheath, a view further developed by Mackeown and Compton.¹⁵

Much work has been done upon the relation between the potential drop at the cathode and the ionization potentials of the gases or vapors which emit radiations when the molecules or atoms are struck by the electrons. Electron densities have also been related to the intensities of lines or bands emitted.¹⁶ Nottingham states the cathode drop of 20 volts in the copper arc to correspond with the second ionization potential of copper vapor. In the cadmium arc, the drop, 8.4 volts, agrees with the ionization potential of cadmium. In the thallium arc, the drop was slightly higher than 6.08 volts, the ionization potential of thallium. In the carbon arc, the cathode fall of 5 volts agreed fairly well with the ionization potential (4.4 volts) of the cyanogen molecule. It may be noted, however, that others report the cathode drop of the carbon arc as 9 volts. That the electrons in the arc plasma could have the necessary velocities to give the required excitation energies implies that the electrons must have a greater velocity of agitation than might be expected from the potential gradient between collisions. The velocity of agitation of the electrons implies an "electron temperature." By the use of the Langmuir probe methods, Nottingham¹⁷ found this temperature to be 6000° for the cadmium arc, 8000° for the thallium arc and 19,000° for the copper arc, or sufficient to account for the observed intensities of the emitted lines.¹⁸

In the course of his work on arc temperatures, Nottingham¹⁹ developed a photographic method for finding the area of the hot spot on the cathode from which the arc passes. This area appeared to increase in proportion to the total current, so that the current density remained constant. In the arc itself, a magnetic field due to the current tends to concentrate the discharge about a longitudinal axis in its center.²⁰

The vapors distilled from metallic arcs have been studied by Rayleigh²¹ and by Berkey and Mason.²² Matter is lost from the cathode of an iron arc. The decrease in weight of the latter is not proportional to the current alone, but depends

¹¹ Hagenbach, A., and Langhein, K., *Arch. Gen.*, **461**, 329 (1918); Tanberg, R., and Berkey, W. E., *Phys. Rev.*, **38**, 296 (1931).

¹² Slepian, J., *Phys. Rev.*, **27**, 407 (1926); Seeliger, R., *Physik. Z.*, **27**, 22 (1926); **31**, 691 (1930).

¹³ Nicol, J., *Proc. Roy. Soc.*, **82A**, 29 (1909); Stolt, H., *Z. Physik*, **26**, 95 (1924).

¹⁴ Langmuir, I., *Gen. Elec. Rev.*, **26**, 735 (1923); *Z. Physik*, **46**, 282 (1927).

¹⁵ Mackeown, S. S., and Compton, K. T., *J. Am. Inst. Elec. Eng.*, **46**, 1192 (1927). See, however, Slepian, J., and Haverstick, E. J., *Phys. Rev.*, **33**, 52 (1929), and Mason, R. C., *Ibid.*, **38**, 427 (1931).

¹⁶ See for the copper arc measurements, Bramhall, E. H., *Phil. Mag.*, **13**, 682 (1932); Ornstein, L. S., and Vermeulen, D., *Z. Physik*, **70**, 564 (1931); Schmidt, R. W., *Z. Physik*, **106**, 35 (1937); Robertson, R. M., *Phys. Rev.*, **53**, 578 (1938).

¹⁷ Nottingham, W. B., *J. Frank. Inst.*, **206**, July, 1928; **207**, March, 1929; **208**, 192 (1929).

¹⁸ See, however, Bramhall, E. H., *Phil. Mag.*, **13**, 682 (1932). These relations have been discussed more exactly in the positive columns of low pressure gas discharges.

¹⁹ Nottingham, W. B., *J. Frank. Inst.*, **205**, 811 (1928).

²⁰ Northrup, E. F., *Phys. Rev.*, **24**, 474 (1907).

²¹ Rayleigh, Lord, *Proc. Roy. Soc.*, **112A**, 14 (1926).

²² Berkey, W. E., and Mason, R. C., *Phys. Rev.*, **38**, 943, 1783 (1931).

also upon the cooling of the cathode.²³ The whole surface adjacent to the bright spot contributes to the loss. This vaporization of the electrodes makes their nature of particular importance in determining the potential difference across an arc of given length, and in obtaining the constants in the modified Ayrton equation. The transport of luminous material in the arc has been studied by measuring the variations in the intensities of the spectral lines in different portions of the arc,²⁴ as well as by other methods.²⁵ Very high velocities have been observed.²⁶

SPECTROGRAPHIC ARCS^{26a}

An arc between iron electrodes generally is employed in spectroscopy. Baly²⁷ used a horizontal arc with the iron poles mechanically rotated in opposite directions. The arc was stated to be capable of giving long exposures. This was a modification of a device of Crew and Tatnall²⁸ in which one electrode comprised a rapidly revolving disk mounted on the armature of a motor and carrying on its periphery small pieces of the metal whose spectrum was to be observed. The other electrode was a rod of the same metal mounted on a fine-cut screw so that the position of the electrode could be accurately adjusted.²⁹

The Pfund arc,³⁰ used as a steady source for the measurements of wave-lengths of the iron arc, is vertically mounted. In operation, the iron arc makes a transition from a high voltage stage to a low voltage stage with currents of about one ampere. Cady and Arnold³¹ find the excess potential in the high voltage stage to lie in the anode fall. The iron arc burns at low voltages in impure argon, helium or neon, but cannot be struck in these gases if the latter are rigidly purified.³²

An enclosed iron arc described as a convenient source for the standardization of spectral lines³³ emits a discharge in an inert gas. The latter is maintained at atmospheric pressure. In this manner one electrode is heated to a temperature sufficient to provide enough metal vapor to yield the iron spectrum. At least one electrode is compacted of sintered pure iron or iron compounds and contains an electron-emitting substance such as barium or calcium oxide. Titanium, tungsten, molybdenum and chromium must be absent to prevent confusion in reading the spectrum. A window for transmitting the radiations is placed on a tubular extension of the bulb.

Data on exact wave-lengths of the standard lines of the iron arc have been

²³ Schmuck, H., and Seeliger, R., *Physik. Z.*, **29**, 864 (1928). See also Laudet, G., *Compt. rend.*, **192**, 202 (1931), and Kirschstein, B., *Wiss. Vortr. Siemens-Werke*, **16**, 69, 72 (1937), *Chem. Abs.*, **31**, 7341 (1937), **32**, 2034 (1938).

²⁴ Ornstein, L. S., and Koopmans, T., *Proc. Acad. Sci. Amsterdam*, **34**, 1099 (1931), *Chem. Abs.*, **26**, 4755 (1932).

²⁵ Tanberg, R., *Phys. Rev.*, **35**, 1080 (1930).

²⁶ See, e.g., Slepian, J., and Mason, R. C., *Phys. Rev.*, **37**, 779 (1931), Compton, K. T., *Ibid.*, **36**, 706 (1930).

^{26a} For a summary of recent theory, Rollwagen, *Spectrochem. Acta*, **1**, 66 (1939).

²⁷ Baly, E. C. C., "Spectroscopy," Vol. 2, p. 91, London, Longmans Green and Co., 1927.

²⁸ Crew, H., and Tatnall, R., *Phil. Mag.*, **38**, 379 (1894).

²⁹ See also Neuhaus, C. J., *Am. Soc. Testing Materials*, Preprint No. 51 (1938), *Chem. Abs.*, **32**, 6105 (1938).

³⁰ Pfund, A. H., *Astrophys. J.*, **27**, 296 (1908).

³¹ Cady, W. G., and Arnold, H. D., *Physik. Z.*, **8**, 890 (1907).

³² Doan, G. E., and Myer, J. I., *Phys. Rev.*, **40**, 36 (1932).

³³ British P. 401,509, Nov. 16, 1933 (Patent Trenhand Gesellschaft für elektrische Glühlampen, assigned to General Electric Co., Ltd.), see also Piani, M., and Rompe, R., *Z. tech. Physik*, **13**, 134 (1932).

reported by Babcock³⁴ and by Burns and Walters,³⁵ with particular reference to the vacuum arc.*

ULTRAVIOLET SOURCES FOR PHOTOCHEMICAL PROCESSES

Temperatures and energies emitted in small tungsten arcs have been studied by de Groot.³⁸ Moore³⁹ employs electrodes of an alloy composed essentially of tungsten with 1-5 per cent of titanium and 0.25-2.0 per cent of chromium. The tungsten arc between rods of 6.4 mm. diameter is rather unsteady and hard to keep in focus because of the formation of a crust of oxide around the electrode. It is weak in rays of less than 2300A, from which wave-length there is a gradual increase in intensity to a maximum at 4500A.

Arcs carrying 6 amperes between 12 mm. nickel rods are said to provide quiet-burning sources of ultraviolet, emitting strongly at 2300 and at 3500A.⁴⁰ Macdonald⁴¹ produces ultraviolet rays by means of an arc created in a vacuum from electrodes of gold alloyed with copper or silver. Nagaoka and Suguira⁴² described an arc in which the cathode was a carbon rod coated with barium or strontium oxide, the rod being sheathed in a silica tube. Various metals or salts in a similar silica tube served as anode. The arc operated in a vacuum and at 1500 volts produced rays which penetrated aluminum foil. Vaporization of the anode metal, short life of the arc, and the necessity of cooling the system and pumping to maintain vacuum were among the reported disadvantages of this arc. Albers⁴³ described an apparatus for maintaining an enclosed beryllium arc in any atmosphere at reduced or elevated pressures.

THE CARBON ARC

The carbon arc was discovered by Sir Humphry Davy, between 1802 and 1808. He employed a 2000-plate voltaic battery as source of current and obtained an arc three inches long. The development of carbon arcs has followed two chief paths. One is the design of steady, very brilliant arcs for motion-picture projection or for air-port illumination. The second has been concerned with methods for altering the distribution of the intensity of the radiation within various spectral regions to meet special demands of industrial photochemistry. Also, the carbon arc is utilized for therapeutic purposes. Much of the progress has been due to alterations in the carbon electrodes.

An early advance consisted in the introduction of a central core of a soft, neutral composition, which stabilizes the arc stream and prevents the latter from shifting

* What is known as the pole-effect is a slight difference in the wave-lengths of many lines when the arc is examined near the poles or at the center.³⁹ The pole-effect does not affect ordinary analytical methods and is of importance only in precise spectrographic work. In some instances, revolving electrodes may be employed.³⁷

³⁴ Babcock, H. D., *Astrophys. J.*, **67**, 240 (1928).

³⁵ Burns, K., and Walters, F. M., Jr., *Pub. Allegheny Observatory*, **6**, 159 (1929); *Chem. Abs.*, **23**, 4886 (1929).

³⁶ St. John, C. E., and Babcock, H. D., *Astrophys. J.*, **42**, 231 (1915).

³⁷ Sventitski, N. S., *Zavodskaya Lab.*, **6**, 325 (1937); *Chem. Abs.*, **31**, 7762 (1937).

³⁸ de Groot, W., *Physica*, **5**, 121, 234 (1925); *Chem. Abs.*, **19**, 2449, 3215 (1925). For line measurements, see Laun, D. D., *Phys. Rev.*, **48**, 572 (1935).

³⁹ Moore, W. G., U. S. P. 1,872,322, Aug. 16, 1932; *Chem. Abs.*, **26**, 5857 (1932). Note also Blake, G. G., *British P.*, 279,680, Jan. 4, 1927.

⁴⁰ Coblenz, W. W., Dorcas, M., and Hughes, C. W., *Sci. Papers, Bureau of Standards*, **21**, No. 539, p. 547 (1926).

⁴¹ Macdonald, R. F., *British P.* 206,588, Aug. 9, 1922; *Chem. Abs.*, **18**, 1090 (1924).

⁴² Nagaoka, H., and Suguira, Y., *Astrophys. J.*, **57**, 86 (1923).

⁴³ Albers, V. M., *J. Opt. Soc. Am.*, **19**, 146 (1929).

about the rim of the crater. Coating the carbons with copper or other metals lessens overheating. The light from either the solid or the neutral-cored carbon arc (on direct current) comes almost entirely from the crater of the positive carbon, little being derived from the arc stream or the tip of the negative carbon. With alternating current, there are two craters of light, but the brilliancy and efficiency are somewhat less than that secured with direct current.

There have been developments in the application of refractory coatings. Thus, the electrodes may be placed in a silica tube and heated to 700° in a current of silicon tetrafluoride at a pressure slightly above atmospheric to form a non-oxidizable coating which retards combustion.⁴⁴ Other coatings of silicon or tungsten carbides⁴⁵ or of sprayed chromium on the carbon⁴⁶ have been described. In some instances, the carbon first is covered with silvered copper, and the whole sprayed with chromium. The use of a cellulose lacquer coating to prevent the absorption of water on the carbon, which causes flickering, has been proposed by Wilson.⁴⁷ As the arc passes, the positive terminal becomes hollowed out to a crater, while the negative terminal remains pointed. According to Griffith, Taylor and Jack⁴⁸ the flame of the arc contributes most of the radiation which is effective therapeutically. The efficiency of the arc increases to a limiting value with flame length, above which the efficiency is independent of flame length. The ultraviolet emission is a function of the watts consumed in the flame of the arc.

A high intensity carbon arc, intended for motion picture projection in large theatres, comprises cored $\frac{1}{8}$ mm. positive carbons (without metallic coatings) and smaller copper-coated negative carbons.⁴⁹ The arc is operated with a horizontal positive carbon, continuously rotated to maintain a well-formed crater. The cathode is placed at an angle 40-60° below the horizontal. Arc currents of 60 to 190 amperes are employed at 45 to 90 volts, d.c. The spectral energy distribution is said to be similar to that of sunlight. The crater furnishes 70 per cent of the light, the remainder coming from the tail-flame. The color and brilliancy of the light indicate a temperature of 5500°C. Since this is higher than the vaporization temperature of carbon, the source must be other than the solid tip of incandescent carbon. Alternating current high intensity arcs have been developed. High intensity carbons usually are cored with cerium fluoride or some similar material. The very high current densities require the use of oxides, fluorides, etc., in a central rod, embedded in the carbon.⁵⁰ Only difficultly vaporizable substances may be used in the core. Alkalies must be avoided as they are detrimental to the brilliancy of the crater.⁵¹ Beck has described the construction of a negative electrode for high intensity arcs.⁵²

Temperatures in the arc may be estimated by a study of the intensities of band

⁴⁴ Singleton, W., and Hare, A., British P. 248,167, March 17, 1925 (General Electric Co., Ltd.).

⁴⁵ I. G. Farbenindustrie, German P. 578,501, June 14, 1933.

⁴⁶ C. H. Champion and Co., Ltd., and Champion, C. H., British P. 406,434, March 1, 1934.

⁴⁷ Wilson, W. N., British P. 395,073, July 13, 1933.

⁴⁸ Griffith, H. D., Taylor, J. S., and Jack, J. M., *Brit. J. Radiology*, 23, 203 (1927); *Chem. Abs.*, 21, 3830 (1927).

⁴⁹ Kalb, W. C., *Elec. Eng.*, 53, 1173 (1934); 56, 319 (1937). See also Bassett, P. R., *Trans. Am. Electrochem. Soc.*, 44, 153 (1923). The toxicity of the fumes from such arcs appears to be due primarily to nitric oxide, carbon monoxide being negligible, according to MacQuiddy, E. L., Tollman, J. P., LaTowsky, L. W., and Bayliss, M., *J. Ind. Hyg. Toxicol.*, 20, 297, 312 (1938); Coltman, R. W., *Ibid.*, 20, 289 (1938).

⁵⁰ Orne, S. W., U. S. P. 1,867,524, July 12, 1932; *Chem. Abs.*, 26, 4544 (1932); Dorcas, M., U. S. P. 1,920,921, Aug. 1, 1933; *Chem. Abs.*, 27, 4746 (1933).

⁵¹ British P. 285,424, June 19, 1929 (Compagnie Lorraine de Charbons pour l'Electricité); see also U. S. P. 1,952,810, March 27, 1934; *Chem. Abs.*, 28, 3317 (1934), and British P. 475,252, Nov. 16, 1937; *Chem. Abs.*, 32, 3280 (1938).

⁵² Beck, H., U. S. P. 1,991,998, Feb. 19, 1935.

spectra.⁵³ Ornstein and Brinkman⁵⁴ concluded from the intensity of the cyanogen bands at 3884 and 4216Å, that the violet kernel of the carbon arc shows a temperature of 6500°K. Lower temperatures of 2950 to 3600° were obtained when the bands of AlO were produced by filling the anode cup with alumina and carbon. Other results indicated the arc gases to have temperatures exceeding those of the electrodes, showing that the high temperature of the gas plays an essential role in the discharge mechanism.⁵⁵ By a method based upon the reflectivity of carbon, Warmuth⁵⁶ calculates the temperature of the positive crater to be 3740°C. Chaney, Hamister and Glass⁵⁷ find the temperature of the positive crater to approach as a limit the sublimation point of pure crystalline graphite. They state the maximum brightness temperature of the carbon crater is probably 3810°K or 40° higher than that found by Waidner and Burgess. The true crater temperature they believe to be between 3925 and 3970°K.

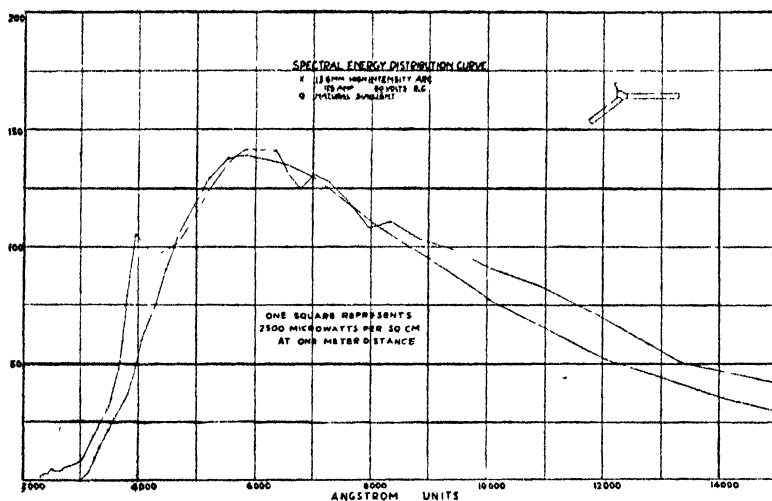


FIGURE 11. Spectral Energy Distribution Curves of Sunlight and High-intensity Carbon Arc (Greider, *Industrial and Engineering Chemistry*)

Ryde⁵⁸ found that in arcs with a positive carbon cored with calcium fluoride and operated at current densities greater than the limiting current densities for ordinary carbons, a bright central core develops in the arc stream. In the central core, the spectra of neutral carbon, nitrogen and oxygen, the Balmer series of

⁵³ v. Engel, A. and Steenbeck, M., [*Naturwiss.* **19**, 212 (1931), *Chem. Abs.*, **25**, 2357 (1931)], use the absorption of x-rays.

⁵⁴ Ornstein, L. S., and Brinkman, H., *Naturwiss.* **19**, 462 (1931); *Proc. Acad. Sci. Amsterdam*, **34**, 33, 498 (1931); *Chem. Abs.* **25**, 3567, 5842 (1931).

⁵⁵ Ornstein, L. S., Brinkman, H., and Vermeulen, D., *Proc. Amsterdam*, **34**, 764 (1931); Ornstein, L. S., *Physik. Z.*, **32**, 517 (1931); Ornstein, L. S., Brinkman, H., and Beunes, A., *Z. Physik*, **77**, 72 (1932); Mason, R. C., *Physica*, **5**, 777 (1938); *Chem. Abs.*, **32**, 8364 (1938). For determinations by other methods see Hörmann, H., *Z. Physik*, **97**, 539 (1935). Lochte-Holtgreven, W., and Maecker, H., [*Z. Physik*, **105**, 1 (1937)] raise the values from cyanogen bands to 7600° for the normal and to as high as 8700° for an over-run arc. See also Khlebnikova, L. Y., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **7**, 1220 (1937); *Chem. Abs.*, **33**, 4866 (1939); Khranova, E. F., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **8**, 176 (1938); *Chem. Abs.*, **33**, 4866 (1939).

⁵⁶ Warmuth, K., *Wiss. Veröffentlich. Siemens-Konz.*, **7**, 307 (1928); *Chem. Abs.*, **23**, 316 (1929).

⁵⁷ Chaney, N. K., Hamister, V. C., and Glass, S. W., *Trans. Electrochem. Soc.*, **67**, 107 (1935).

⁵⁸ Ryde, J. W., *Proc. Roy. Soc. London*, **117A**, 164 (1927).

hydrogen and some argon lines are excited. Of the two chief band systems, *i.e.*, the Swan bands and the cyanogen bands, the former are strongly excited close to and inside the positive carbon, but do not appear at all in the arc stream under normal conditions. The origin of the cyanogen bands is well established, since they are absent when the arc is operated in a gas free from nitrogen. The Swan bands appear to be formed by C_2 .⁵⁹ An increase in current rapidly increases the intensity of the cyanogen bands.

The distribution of energy in the carbon arc operated under various conditions has been determined by Greider,⁶⁰ who employed a quartz monochromator for the region between 2300 and 7000Å and an infrared spectroradiometer between 6000 and 18000Å. The relative energy distribution curves were converted into absolute energy unit curves by a method involving the use of a galvanometer and ther-

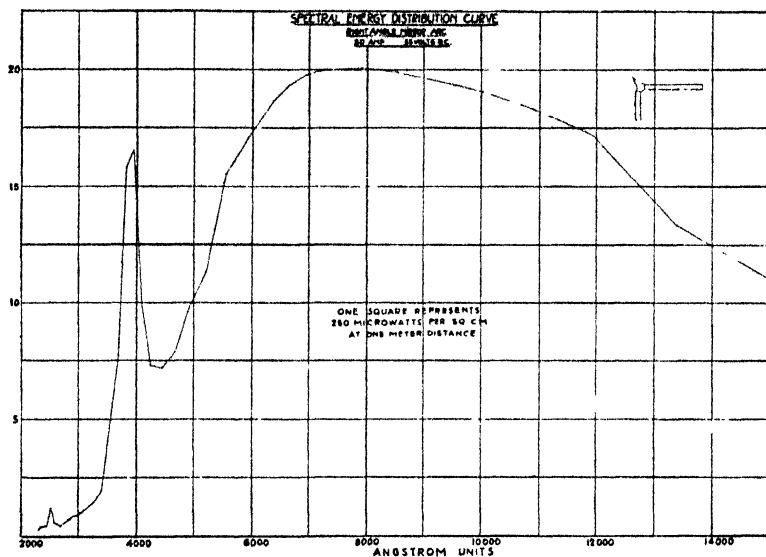


FIGURE 12. Spectral Energy Distribution Curves of Plain-carbon Arc, Burned under Low-intensity Conditions (Greider, *Industrial and Engineering Chemistry*).

mopile.⁶¹ In the curves reproduced in Figures 11 and 12, unit areas represent unit amounts of energy, so that the intensity between any two wave-length limits may be estimated by measuring the corresponding area under the curve.

Figure 11 compares the energy distribution from a 13.6 mm. high-intensity arc operated at 125 amperes and 80 volts d.c. with that of normal sunlight. Each square represents 2500 microwatts per sq cm. at a distance of one meter. The agreement is quite remarkable, the chief difference being in the greater output by the arc of radiations shorter than about 4500Å. The spectrum also extends to a shorter wave-length limit, although this forms but an insignificant fraction of the total radiation from the arc.

⁵⁹ Johnson, R. C., *Nature*, **116**, 539 (1925); Johnson, R. C., and Asuudi, R. K., *Proc. Roy. Soc., London*, **124A**, 668 (1929).

⁶⁰ Greider, C. E., *Ind. Eng. Chem.*, **23**, 508 (1931), for a discussion of the methods employed in such measurements, see Chapter 7.

⁶¹ Greider, C. E., and Downes, A. C., *Trans. Illum. Eng. Soc.*, **25**, 378 (1930), **27**, 637 (1932). See also Mandel'shtam, S. L., *Compt. rend. acad. sci. U.R.S.S.*, **18**, 559 (1938).

The energy distribution of the plain carbon arc with poles at right angles and carrying 30 amperes at 55 volts is shown in Figure 12 in which each square represents but one-tenth of the energy of the previous figure. This arc burns at a lower temperature, so that the total intensity is lower, and the intensity maximum occurs at a longer wave-length. There appears also a larger amount of the line or band spectrum from the arc stream, giving peaks at 2500 and 3900Å. When a plain vertical carbon arc is utilized, there is found to be relatively less continuous radiation from the craters. Also the maximum intensity lies much farther toward

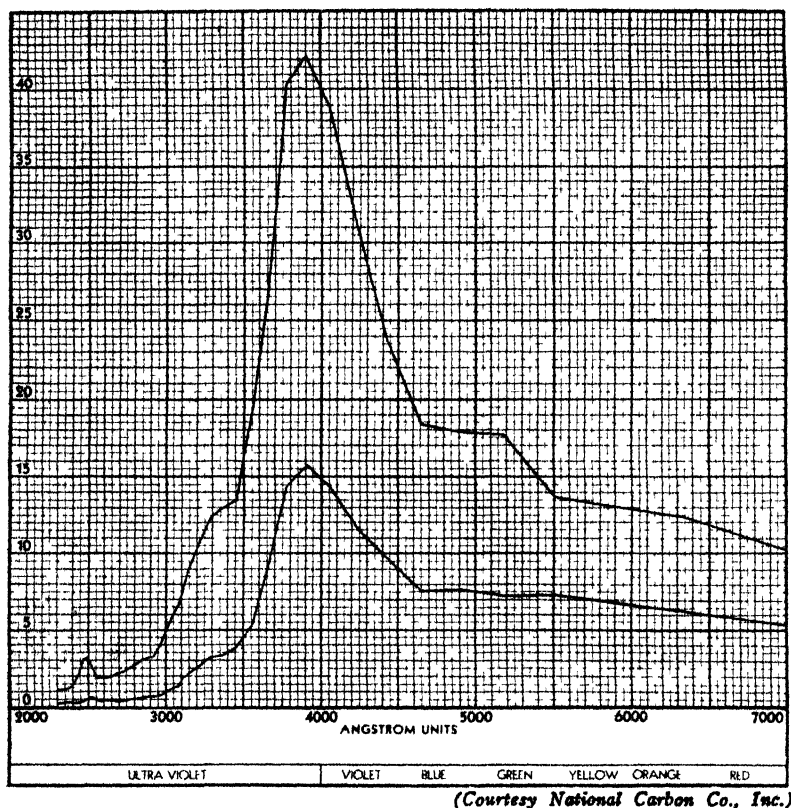


FIGURE 13. Spectral Energy Distribution of Sunshine Carbons.

the infrared than with high intensity carbons. This flame carbon arc may be made into a versatile source of radiation by the addition to the electrode of various substances, which may be vaporized into the arc. The added materials are either distributed throughout the carbon or, more commonly, are concentrated into a central core.

Figure 13 gives the energy distribution of Sunshine carbons which contain cerium in the core. As compared with the neutral core arc, there is a marked increase of energy in the ultraviolet, increasing gradually in intensity from about 2900 to 4000Å. There is a fairly uniform intensity at a much lower level, from about 4500 to 8000Å, due to lines so closely packed together as to yield a nearly continuous spectrum. Beyond about 8000Å the intensity falls off rapidly, practically

all radiation in this area being that from the incandescent poles. Such arcs are especially suitable for photography and photoengraving. Reactions believed to occur within the arc stream or hot electrodes of the cerium carbons have been discussed by Bassett.⁶² These carbons are also suitable for therapeutic arcs in which it is desired to imitate sunlight. The lower and upper curves in Figure 13 refer to the output of the arcs operated with 30 and 60 amperes, respectively. Figures 14, 15, 16, 17, and 18 give similar data for various other therapeutic carbons ("B," "C," "E," "K" and "U" are the trade designations). In each case the output increases much more rapidly than the rate of current increase. Up to about 30 amperes, the output is approximately equal to the square of the current, but at higher currents the rate of output decreases. The "B" carbons contain iron and yield light similar in general distribution to that of the mercury arc.

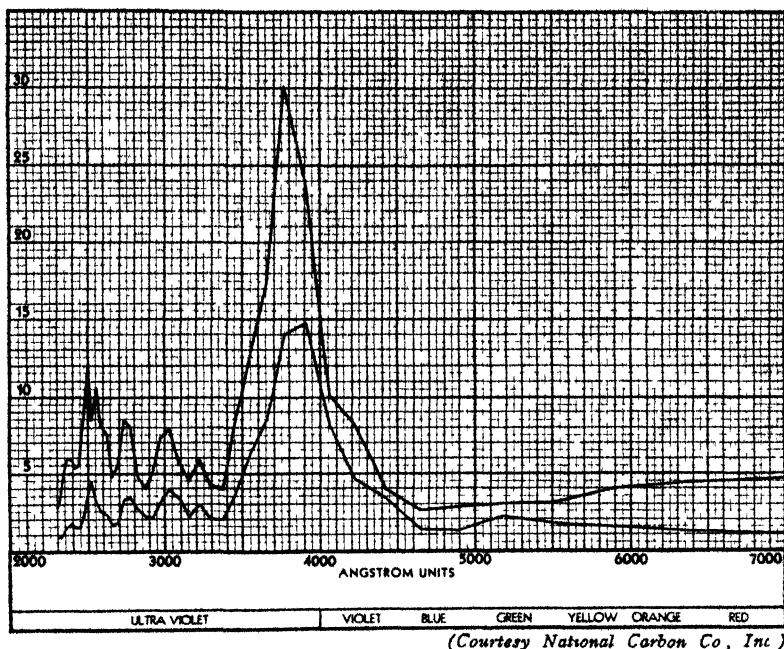
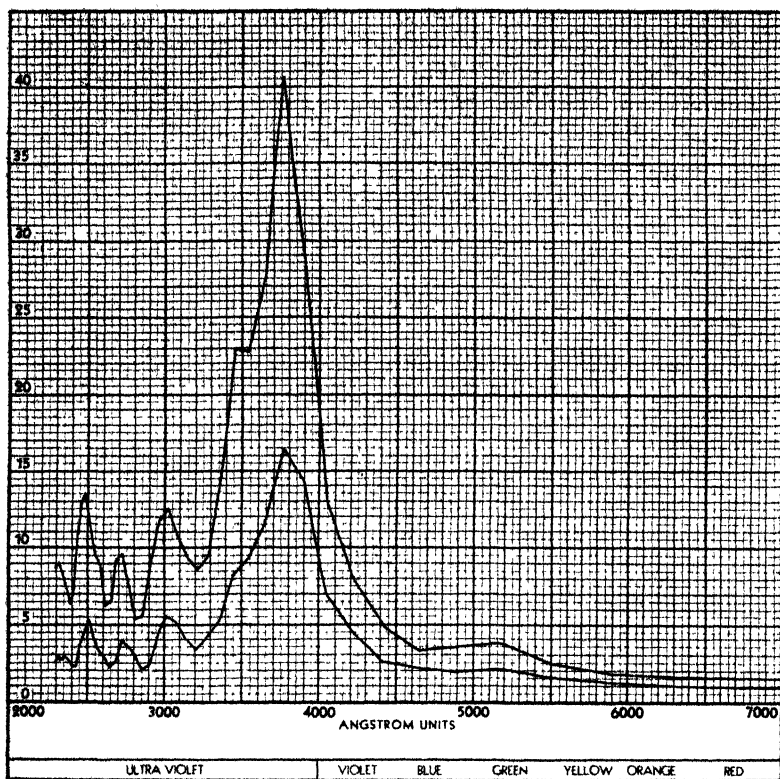


FIGURE 14. Spectral Energy Distribution of Therapeutic B Carbons.

The "C" carbons contain in the core a mixture of metals including iron, nickel and aluminum. Dorcas⁶³ has described the preparation of these electrodes. A hollow shell tube of carbon is formed and baked at 1400°C. Into the tube is then forced the core and the whole heated. These carbons give a series of groups of very intense lines in the ultraviolet, with but a relatively low intensity of energy in the visible region. The infrared radiation follows the general shape of the curve for the incandescence of carbon craters, but is relatively low in intensity. The "C" carbons are used for ultraviolet therapy as they have an even distribution of radiation through the physiologically active range. A 30-ampere "C" carbon arc at 50 volts, a c, is said to give two to seven times as much biologically active ultraviolet energy as do mercury arcs. The "C" carbon is particularly strong in the zone

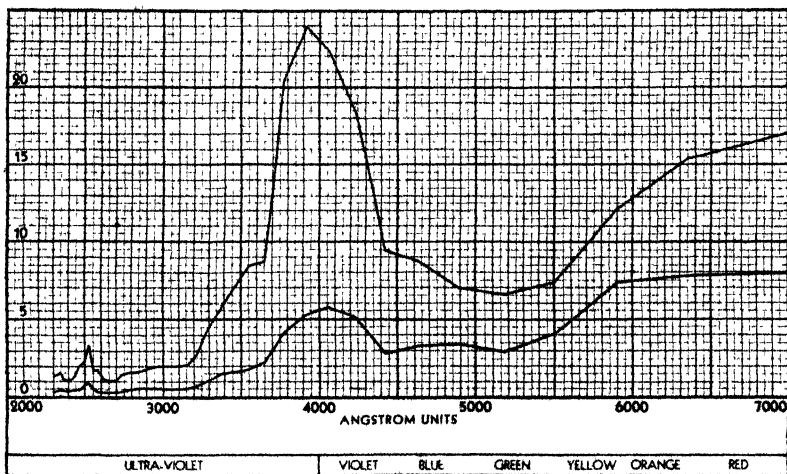
⁶² Bassett, P. R., *Trans Electrochem. Soc.*, **44**, 153 (1923).

⁶³ Dorcas, M. J., U. S. P. 1,862,300, June 7, 1932.



(Courtesy National Carbon Co., Inc.)

FIGURE 15. Spectral Energy Distribution of Therapeutic C Carbons.

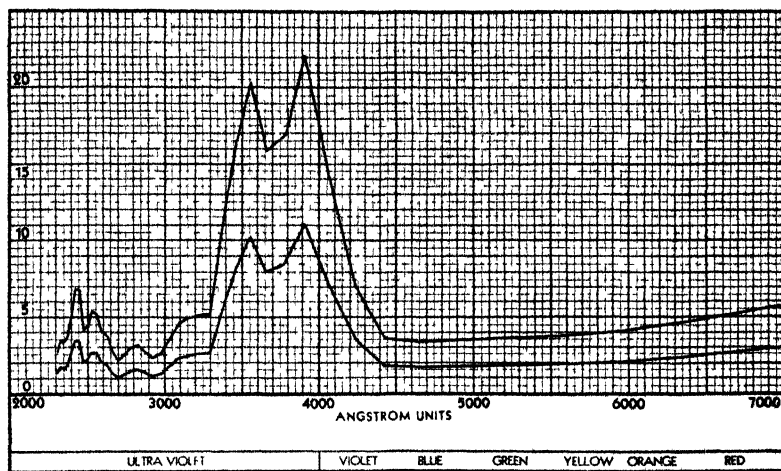


(Courtesy National Carbon Co., Inc.)

FIGURE 16. Spectral Energy Distribution of Therapeutic E Carbons.

of antirachitic radiation (2700 to 3000A) and is the strongest of all therapeutic carbons of the National Carbon Co. series in the tan-producing zone from 3000 to 3200A.

To secure particular energy distributions in the ultraviolet wires of zinc or aluminum may be embedded in holes bored in the carbon. Copper and cobalt usually are added in powder form to the carbon. Cobalt ("K" carbons) gives a very high intensity near 2400A and a peak near 3600 A, with a low intensity in the visible and infrared in comparison with the plain carbon arc. In absolute units the energy is not far different at 9000A and at the 2400A peak. This carbon is said to simulate in effects the Kromayer mercury arc. (See page 126)



(Courtesy National Carbon Co., Inc.)

FIGURE 17. Spectral Energy Distribution of Therapeutic K Carbons.

To secure particularly the region 2800 to 3100A, Greider⁶⁴ employs about equal quantities of iron, chromium, manganese and titanium in the core of the carbon. Arcs with calcium or strontium compounds in the core have relatively little energy in the ultraviolet. The strontium arc ("E" carbons) is used in infrared therapy. The intrinsic brilliance of the flame of all these arcs is relatively low, but the size of the flame is stated to give volume and efficiency.⁶⁵

The effects of various proportions of iron in the anode on the spectrum of the carbon arc have been determined by Reiniers.⁶⁶ With 30 to 90 per cent of iron, the cyanogen band could still be detected, but most of the other bands disappeared when 2 per cent of iron was present, with the exception of those at 5152-5159A. The latter can still be detected with 25 per cent iron in the carbon.

Peczalski⁶⁷ has shown that the spectrum of the internal layers of an arc salted with calcium fluoride consists principally of calcium fluoride bands.⁶⁸ Reiter and

⁶⁴ Greider, C. F., U. S. P. 1,920,255, Aug. 1, 1933 (to National Carbon Co.). See, however, O'Brien, B., U. S. P. 2,121,882, June 28 1938, *Chem. Abs.* 32, 6353 (1938).

⁶⁵ Extensive studies of the emission of various carbons have also been made at the Bureau of Standards. Coblentz, W. W., Dorcas, M. J., and Hughes, C. W., *Sci. Papers Bureau Standards*, 21, No. 539 (1926); Coblentz, W. W., *Am. J. Electrotherapeutics and Radiology*, 63, 455 (1925).

⁶⁶ Reiniers, J. H., Jr., *Verslag Akad. Wetenschappen Amsterdam*, 33, 655 (1924); *Chem. Abs.*, 19, 2300 (1925).

⁶⁷ Peczalski, T., *Compt. rend.*, 199, 405 (1934); Szulc, N., *Ibid.*, 201, 48 (1935).

⁶⁸ For details of the preparation of carbon electrodes containing calcium fluoride, see M. and V. Arnone, *British P.* 247,831, Feb. 25, 1926; *Chem. Abs.*, 21, 536 (1927); and also Orne, S. W., U. S. P. 1,867,524, July 12, 1932; *Canadian P.* 310,628, April 21, 1931.

Gabor⁶⁹ describe an arc in which at least one electrode containing silver is used in conjunction with various filters. This arc was stated to produce a strong spectrum between 3300 and 3600A, lines of wave-lengths less than 3200A being practically absent. The arc was intended for use in the stimulation of plant growth. (See, however, Chapter 44.)

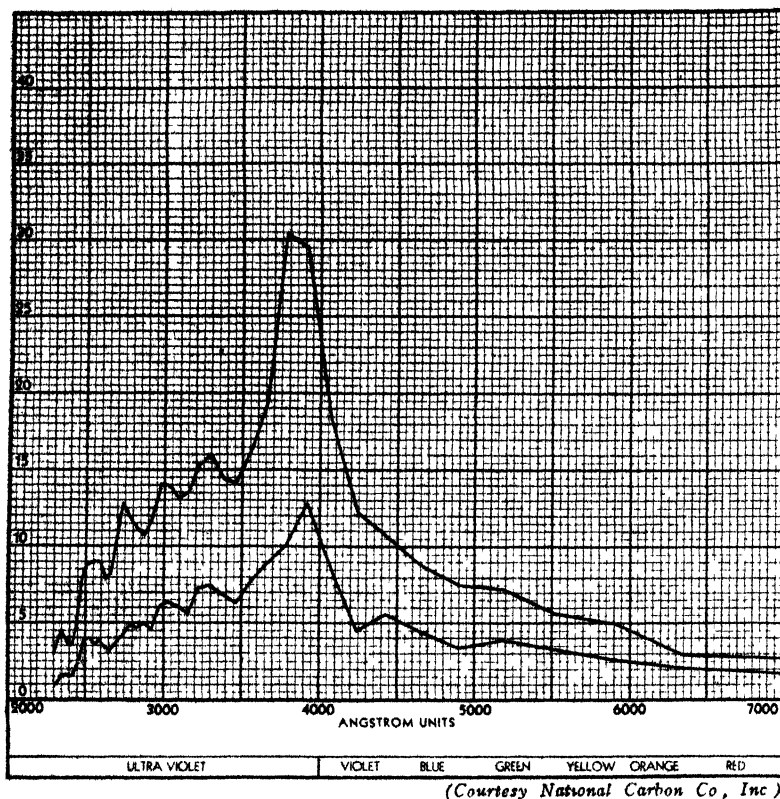


FIGURE 18 Spectral Energy Distribution of Therapeutic U Carbons.

For therapeutic radiations, Chesney⁷⁰ employs carbon with iron carbide and at least two ferroalloys of metals, such as uranium, tungsten, vanadium, molybdenum, yttrium, titanium, tantalum and zirconium, having complementary spectra rich in ultraviolet. E. and O. Conradty⁷¹ add bismuth or a salt of bismuth to the core of a carbon arc.

Lavoisier⁷² uses as one electrode a dehydrated and glazed mixture of zirconia and yttria. Volmer⁷³ uses electrodes of metal oxides, nitrides, carbides or silicates.

⁶⁹ Reiter, T., and Gabor, D., U. S. P. 1,856,969, May 3, 1932 (to Siemens and Halske, A.-G.), *Chem. Abs.*, 26, 3447 (1932).

⁷⁰ Chesney, J., U. S. P. 1,838,741, Dec. 29, 1931 (to U V Generator Corp.); *Chem. Abs.*, 26, 1202 (1932).

⁷¹ Conradty, E., and Conradty, O., French P 710,913, Feb. 6, 1931; *Chem. Abs.*, 26, 1526 (1932).

⁷² Lavoisier, I. J., U. S. P. 1,682,847, Sept. 4, 1928 (to Burdick Corp.); *Chem. Abs.*, 22, 3848 (1928).

⁷³ Volmer, M., British P. 418,988, Oct. 29, 1934; U. S. P. 2,074,600; *Chem. Abs.*, 29, 2454 (1931).

The metals suggested include zirconium, magnesium or aluminum with the addition of ferric oxide. Moore and Hole⁷⁴ use powdered tungsten sintered with iron and titanium and add other metals to supply radiations in any desired part of the spectrum.

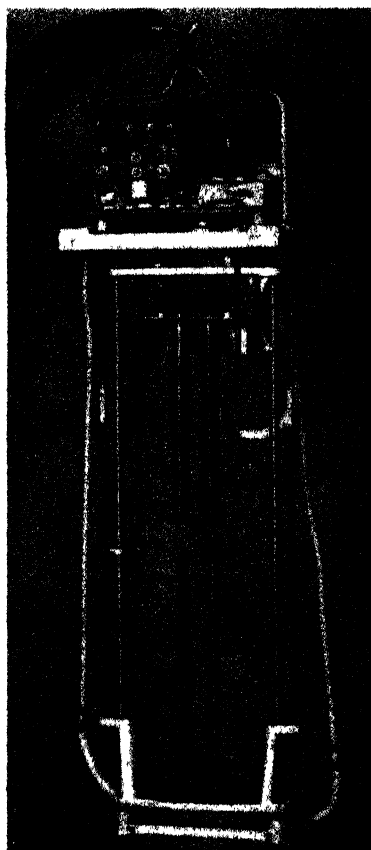


FIGURE 19.

Industrial Carbon Arc.

(Courtesy National Carbon Co., Inc.)

Unusual designs of carbon arcs have been proposed. Pauthenier⁷⁵ used a rotating arc and Pierucci⁷⁶ employed an electrolyte as one electrode of an alternating current carbon arc. Rocard and de Rothschild⁷⁷ direct gas currents along the electrodes. According to Gauthier, Le Bozec and Dubois,⁷⁸ a cathode for rotary flame arcs comprises a hollow annular ring in which a cooling liquid flows con-

⁷⁴ Moore, W. G., and Hole, K. W., British P. 450,552, July 20, 1936; Moore, W. G., British P. 245,872; *Chem. Abs.*, 21, 363 (1927).

⁷⁵ Pauthenier, *Compt. rend.*, 180, 1834 (1925).

⁷⁶ Pierucci, M., *Nuovo cimento*, 12, 1 (1935); *Chem. Abs.*, 29, 3607 (1935).

⁷⁷ Rocard, Y. A., and de Rothschild, P., British P. 287,160, March 17, 1927.

⁷⁸ Gauthier, G., Le Bozec, L., and Dubois, R., U. S. P. 1,793,605, Feb. 24, 1931; *Chem. Abs.*, 25, 2061 (1931).

tinuously. An apparatus for producing an electric arc in which a gaseous hydrocarbon is led between two concentric carbon electrodes has been described.⁷⁹

For commercial arcs intended as photochemical sources, some type of automatic feed for one or both of the poles is necessary to keep the arc length constant though the pole materials suffer destruction. In some instances an electromagnetic device is employed which alters the distance between poles as the current through the arc

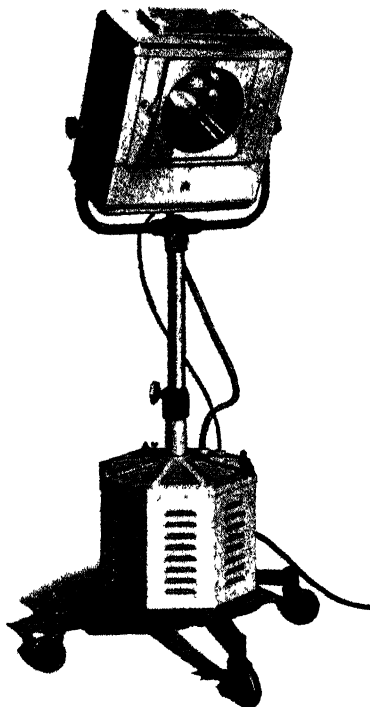


FIGURE 20.

Eveready Model A-2 Carbon Arc
Lamp.

(Courtesy National Carbon Co., Inc.)

changes. A method based upon thermostatic control has been advocated by Patterson.⁸⁰ Photoelectric control⁸¹ has also been proposed.⁸²

Industrial arc installations have been developed by the National Carbon Co. (Figure 19.)⁸³ Such arcs are reported to operate for ten hours or more without attention, and to be capable of remote or automatic control. It is claimed the ultraviolet shorter than 4000Å can be produced by this arc in commercial quantities with a switchboard efficiency of over 12 per cent. A typical medium-sized unit uses 3

⁷⁹ Presslicht-Patent-Verwertungsgesellschaft, German P. 579,682, June 29, 1933; *Chem. Abs.*, 28, 980 (1934).

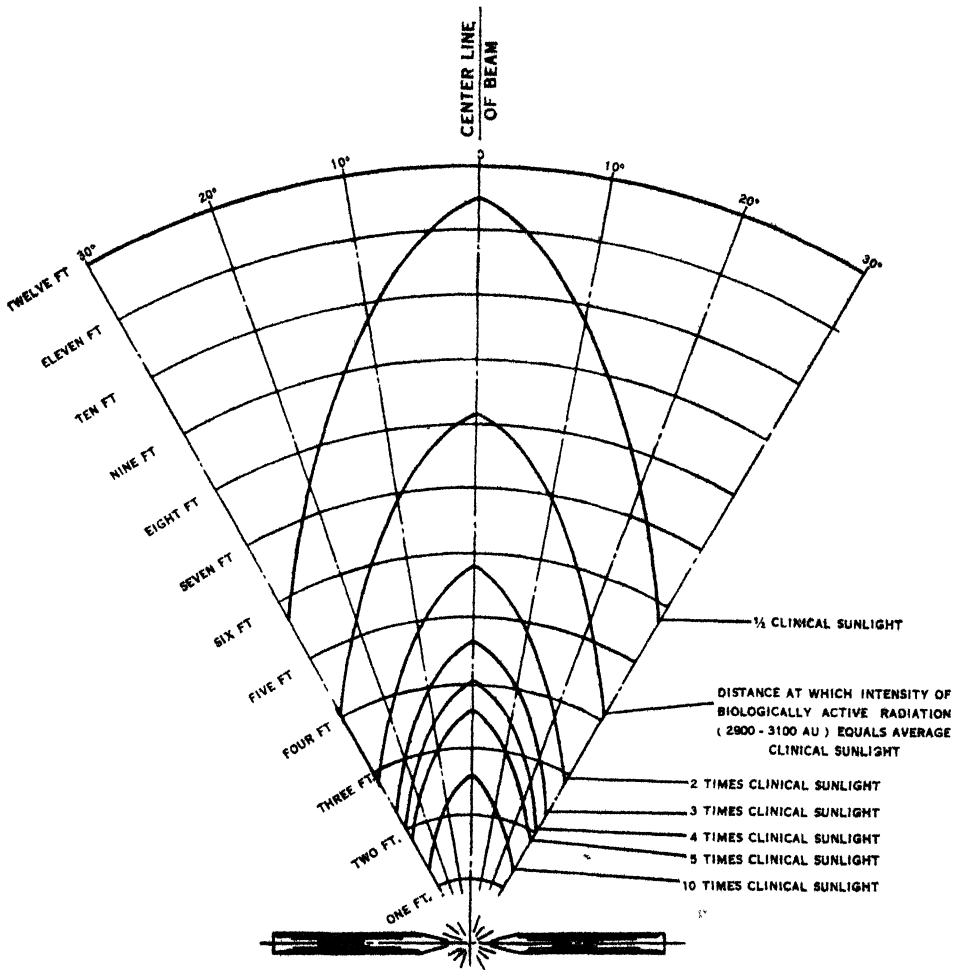
⁸⁰ Patterson, M. L., U. S. P. 1,778,770, Oct. 21, 1931; *Chem. Abs.*, 25, 6 (1931).

⁸¹ Lennox, E. A., British P. 383,853, Nov. 24, 1932.

⁸² Other details of mechanical construction and control: Tappan, C., British P. 412,844, July 5, 1934; Boardman, R., British P. 372,552, May 1, 1931; Taylor, A., and Heathcote, R., British P. 416,170, Sept. 13, 1934; Woerner, H. B., U. S. P. 1,705,798, March 19, 1929; Siemens-Schuckert Werke, British P. 390,624, April 13, 1933; Robinson, F. W., British P. 379,524, Sept. 1, 1932; Zeiss Ikon, A.-G., British P. 381,452, Oct. 6, 1932; 414,316, Aug. 2, 1934; 405,597, Feb. 8, 1934; Hall, B. J., British P. 396,876, Aug. 17, 1933; Anderson, N. J., and Rigby, R., Ltd., British P. 391,059, April 20, 1933; Cricks, Rigby and Rigby, Ltd., British P. 400,692, Nov. 2, 1933; Volmer, M., U. S. P. 2,004,680, June 1, 1935; British P. 418,988, Oct. 29, 1934.

⁸³ Dorcas, M. J., *Ind. Eng. Chem.*, 22, 1244 (1930).

kilowatts (59 volts, 60 amperes) directly from a 220-volt a.c. line through transformers. With "C" carbons, it would give about 50×10^{-6} watt per square millimeter (at one meter horizontal distance from the arc) of radiation shorter than 6500A. About half of this radiation is in the ultraviolet range. Each square meter (and there are 12.5 such around the arc) can be irradiated with 25 watts of ultraviolet. Such units are of value in the food and stock- and poultry-feed industries.



(Courtesy National Carbon Co., Inc.)

FIGURE 21. Curves of Uniform, High-intensity Sunshine Carbons.

Arc lamps with special housings are available (Figure 20) equipped with a removable Corex D glass filter for lessening the output of radiations shorter than 2900A. The lamp uses 115-volt, 60-cycle alternating current. Figure 21 indicates the intensities of the 2900 to 3100A radiations at various positions with respect to the center of the beam, as compared with their intensities in average sunlight. A simpler form of arc lamp (Figure 22) is also utilized. These lamps may be equipped

with adaptors and applicators for irradiation of small areas. (Figure 23.) Large motor-fed solarium units (one-arc, two-arc and four-arc types) make possible the treatment of from 18 to 20 patients at one time (Figure 24) and are in use in many hospitals, schools and sanatoria. Such units,⁸⁴ also adapted to clubs and swimming pools, use carbons 12 feet long. The arc burns between only one pair of carbons at a time, shifting to another set every half hour as the carbons burn back. One trim

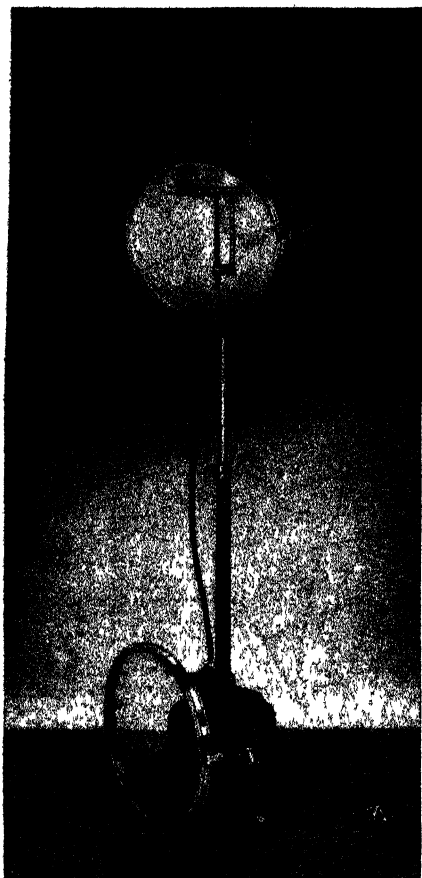


FIGURE 22.

Eveready Model L 1 Lamp

(Copyright National Carbon Co., Inc.)

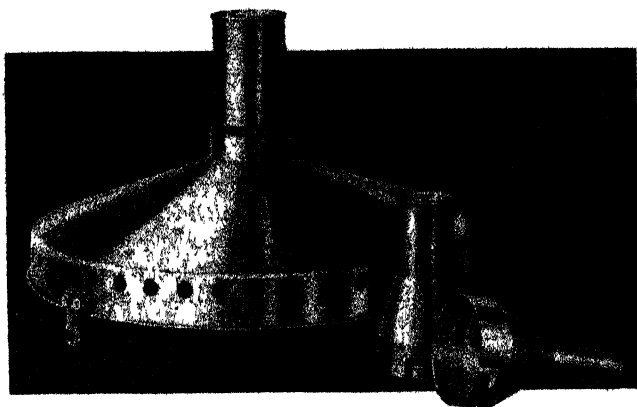
of carbons burns continuously for 12 hours if operated at 45 amperes, ten hours at 60 amperes or 8 hours at 90 amperes.

An arc for splitting hydrocarbon gases to acetylene and hydrogen and for synthesizing hydrogen cyanide has been described.⁸⁵ The zinc-graphite arc has been employed under liquids as a reducing agent.⁸⁶ Under carbon disulfide, the optimum yield of carbon subsulfide was almost 50 per cent of that represented by the reaction:

⁸⁴ Kalb, W. C., *J. Am. Inst. Elec. Eng.*, **49**, 1031 (1930).

⁸⁵ Soc. pour l'ind. chim. Bâle, German P. 607,331, Dec. 21, 1934; British P. 389,761. See also Briner, E., Desbaillets, J., and Faillard, H., *Helv. Chim. Acta*, **21**, 115 (1938).

⁸⁶ Stock, A. Brandt, A., and Fischer, H., *Ber.* **58B**, 643 (1925).



(Courtesy National Carbon Co, Inc)

FIGURE 23 Adaptor and Applicators for Model L-1 Lamp.



FIGURE 24 Solarium Carbon-Arc Equipment.

$3\text{CS}_2 + 4\text{Zn} \rightarrow \text{C}_3\text{S}_2 + 4\text{ZnS}$. With silicon tetrachloride, a stationary aluminum cathode and movable zinc anode, the main reaction at -55° to -15° consists in the production of zinc chloride and silicon, a minor portion of the silicon tetrachloride being converted into hexachlorodisilane. Under similar conditions, phosphorus trichloride yields yellow phosphorus and zinc chloride, together with small amounts of phosphorus dichloride, P_2Cl_4 . Boron trichloride is converted into boron; to a minor extent a chloride, B_2Cl_4 , is produced but the latter was not freed completely from silicon tetrachloride, present as impurity in the boron trichloride used.

Maslowski and Regulski⁸⁷ have produced zinc nitride, Zn_3N_2 , by an arc between zinc electrodes in nitrogen at a pressure below 25 mm.

Under-water operation of an arc has been employed as a method for disintegrating the electrode materials. This is the basis of the Bredig method for the preparation of colloidal suspensions, the details of which have been summarized by Svedberg.⁸⁸ Carter and Campbell⁸⁹ have studied the gaseous products formed during the operation of the carbon arc under water. The average composition of the products was 9.8 per cent carbon dioxide, 18.1 per cent carbon monoxide, 3.3 per cent oxygen, 49.3 per cent hydrogen, 3.2 per cent saturated hydrocarbons and 14.6 per cent residual gas, mostly nitrogen. Finely dispersed graphitic acid also was formed.

Plotnikow⁹⁰ has described accessory equipment for rendering large and small carbon arcs suitable sources for the demonstration of the phenomena of ultraviolet fluorescence. With suitable filters, carbon arcs can be used as sources of infrared for clinical photography.

The carbon arc may also be employed in spectrographic analysis. The material to be tested may be placed within a hole drilled in the lower carbon electrode. Details of analysis are found in manuals of spectrographic analysis.⁹¹ Acheson graphite electrodes, 0.6 mm. in diameter and 5 cm. long, are recommended. Special precautions must be taken in the purification of these electrodes.⁹² Heat treatments usually are employed. The common impurities in the electrodes include vanadium, lithium, strontium, calcium, iron, titanium, barium, aluminum, boron, copper, magnesium, manganese and silicon.⁹³

⁸⁷ Maslowski, K., and Regulski, H., *Compt rend. soc. polonaise phys.*, 3, 87 (1927), *Chem Abs.*, 23, 5114 (1929).

⁸⁸ Svedberg, T., "Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe," Dresden, Steinkopff, 1922.

⁸⁹ Carter, H. D., and Campbell, A. N., *Trans Electrochem. Soc.*, 63, 419 (1933).

⁹⁰ Plotnikow, I., *Z. Elektrochem.*, 35, 434 (1929). For a discussion of syntheses conducted in electric discharges, see Schenk, P. W., *Angew. Chem.*, 50, 535 (1937).

⁹¹ See also Nitchie, C. C., *Ind. Eng. Chem. (Anal. Ed.)*, 1, 1 (1929); Wilhelm, H. A., *Ibid.*, 10, 211 (1938).

⁹² Heyne, G., *Angew. Chem.*, 45, 612 (1932); Moritz, H., *Zentr. Mineral. Geol.*, 1935A, 284; Roach, F., *Nature*, 139, 547 (1937); Russanow, A., *Z. anorg. allgem. Chem.*, 219, 332 (1934); Wehli, D. A., *Nature*, 139, 248 (1937); Staud, A. H., and Rühle, A. E., *Ind. Eng. Chem. (Anal. Ed.)*, 10, 59 (1938); Owens, J. S., Peake, J. S., and Fowler, R. G., U. S. P. 2,117,497, May 17, 1938, *Chem. Abs.*, 32, 4889 (1932). Dow Chemical Co., British P. 496,615, Jan. 3, 1938.

⁹³ Maltby, J. G., *Chem. & Ind.*, 1937, 220; Standen, G. W., and Kovach, L., Jr., *Proc. Am. Soc. Testing Materials*, 35, Pt. 2, 79 (1935); Gatterer, A., *Z. ver. deut. Ing.*, 80, 129 (1936).

Chapter 6

Enclosed Vapor Arcs. The Quartz Mercury-vapor Arc

Enclosed gas and vapor arcs, of which the mercury-vapor arc is the most widely used, differ from the open arcs of the previous chapter in that the enveloping tube or bulb makes the pressure of the gas or vapor in the arc-conducting stream independent of that of the external atmosphere. The transparency of the envelope also limits the radiations available from such arcs. If, as is generally true, the arc vessel contains in liquid or solid form a relatively large quantity of the element, usually mercury, the vapor of which forms the conducting medium for the arc, the vapor pressure will depend upon the operating temperature of the arc. The voltage drop across the arc is dependent, as discussed in the preceding chapter, not only upon the nature of the electrodes, the cathode exerting the predominant effect, but also upon the nature of the gas or vapor, and its pressure. If the vessel contains a supply of unvaporized mercury, the pressure is the vapor pressure of the mercury at the temperature at any time, being very low when the arc is cool, and atmospheric or greater under certain conditions of operation. When the pressure is low, the arc fills the entire tube. When, after a starting period, the pressure of the mercury vapor rises, the arc becomes constricted to a narrow bright luminous stream, surrounded by dark mercury vapor. This absorbs certain of the mercury lines by self-reversal and thus alters the energy distribution between the various mercury lines.

The mercury arc emits predominantly only a few intense lines, superposed upon a weak continuous spectrum, which is neglected in much photochemical work. Under certain conditions, a less-important banded spectrum may be observed. About 6 per cent of the total energy is of wave-lengths less than 2900Å. Figure 25 shows a photograph of the spectrum of a quartz tube mercury arc, and Figure 26 shows the relative intensities of the prominent lines of the spectrum. The relative intensities of these lines are modified by the operating conditions.

The condition of the conducting gas does not limit the current as does the resistance of an electric lamp filament, so that a resistance must always be placed in series with a gaseous conduction discharge in order to operate it.

Since the mercury arc came to be recognized as a reliable source of light of short wave-lengths, the number of types of lamps embodying its use has increased rapidly.

The early forms of the mercury arc were direct outgrowths from the open arcs discussed in the previous chapter and had both electrodes of mercury. In time, it was found advantageous to replace the anode by some other metal. More recently, the tendency has been to avoid the use of mercury cathodes as well, and employ only mercury vapor for the conduction of the discharge. Lamps of this type will be discussed in Chapter 8.

EARLY HISTORY OF THE MERCURY ARC

Perkin¹ considers the observation that a brilliant light is emitted when mercury is vaporized in an electric arc to have been made originally by Wheatstone who, in 1835, described the characteristics of such a light before the British Association. Its illuminating power was not realized, however, until some time later, when in 1852 Jackson secured a patent for a mercury lamp. The latter consisted of carbon electrodes, the lower one of which had a recess to hold a small quantity of mercury, the idea being to provide a non-consuming electrode. Binks about a year later produced and patented a lamp having two mercury electrodes which were enclosed in a glass case. Provision was also made for condensing the vaporized metal to the liquid condition again. Way patented a lamp (in 1856) which was described in the *London Times* of August 3, 1860, with the claim that it produced a more brilliant light than had ever been seen before.

Harrison, in 1857, developed a lamp in which a carbon rod was suspended over a cup of mercury. In another form of lamp, mercury was caused to drop on a carbon rod. Difficulties were encountered in obtaining a steady arc, although Harrison endeavored to overcome these by means of an electro-mechanical device. In 1867, Siemens made a mercury lamp which had a vibrating electrode dipping into a mercury cup. The light of this lamp was, however, of an intermittent nature. Siemens' idea was to employ this lamp for lighting buoys at sea, but apparently the device was never used for this purpose. The next attempt to produce a mercury lamp appears to have been made in 1875 by Prosser. It was a combined carbon and mercury lamp, the object being to overcome flickering, which was an unpleasant feature of the original arc lamps. Among the various other attempts to produce a satisfactory lamp must be mentioned that of Rapiéff in 1879. This lamp contained a condensing chamber for the mercury vapor, and could be started by shaking the mercury or by an electro-mechanical arrangement.

In 1892, Arons showed that an arc could be produced by passing a direct current through mercury in an evacuated tube. The Arons lamp, which was five feet long, was started by tilting and, therefore, must have required a very large quantity of mercury. According to Axmann,² the later types of mercury vapor lamps are based on Arons's investigations upon low-pressure arcs. Thus, in 1892, Dowsing and Keating made a lamp in which an alternating current was passed through a Geissler tube containing mercury. They found it advisable to warm the mercury in order to vaporize it before starting the lamp.

The object of most of the early workers was the production of a lamp for visible illumination. The first lamp to attract attention in this connection was one displayed by Peter Cooper-Hewitt before the American Institute of Electrical Engineers at a meeting in April, 1901.³ This lamp, the result of long experimenting, is said to have been installed first in the composing rooms of the *New York Evening Post* in 1903. Many practical difficulties, such as the inherent instability of the arc, changes in mercury vapor pressure with operating temperature, and distillation of the mercury from certain portions of the lamp, were encountered. Cooper-Hewitt later devised a lamp in which the mercury was cooled and condensed at about the same speed as that at which it vaporized.

The development of the lamp as an illuminating source for factories and drafting rooms lies beyond the scope of this book, except insofar as modifications have been successfully applied to the mercury arc in a quartz tube employed for ultraviolet emission. The reader interested in the development of the Cooper-Hewitt lamp, which is a long arc operating at a low mercury-vapor pressure, should consult the articles by Buttolph⁴ of the Engineering Department of the General Electric Vapor Lamp Co. He points out that during the years 1902-07, the condensing chamber

¹ Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911).

² Axmann, Z. *Phys. diätetische Ther.*, **13**, 470 (1909 10)

³ Buttolph, L. J., *Trans. Electrochem. Soc.*, **65**, 143 (1934).

⁴ Buttolph, L. J., *Gen. Elec. Rev.*, **23**, 741, 858 (1920), *Rev. Sci. Instruments*, **1**, 487 (1930); *Trans. Electrochem. Soc.*, **65** (1934), 143, *Trans. Illum. Eng. Soc.*, Preprint, 1932; **30**, 147 (1935). (See also, Ferguson, J. B., "The Quartz Mercury Vapor Lamp" London Lewis and Co., Ltd.; and also Pierce, R. F., *Illuminating Engineer*, **6**, 133 (1911).

THE QUARTZ-LIGHT SPECTRUM

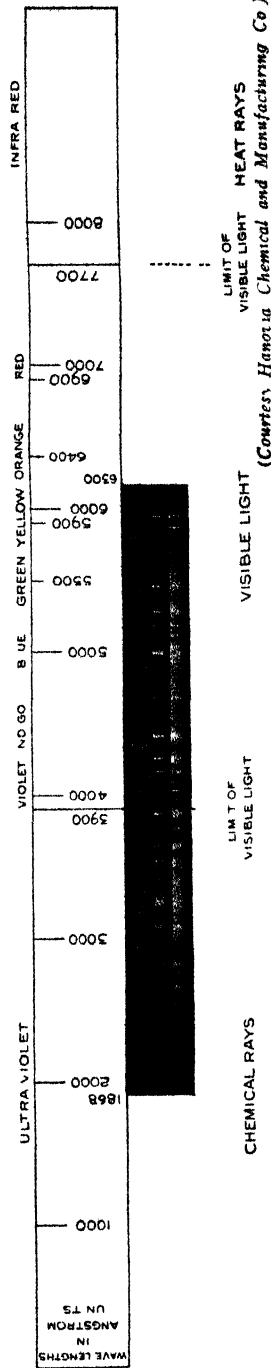


FIGURE 25 Spectrogram of Quartz-Tube Mercury Arc.

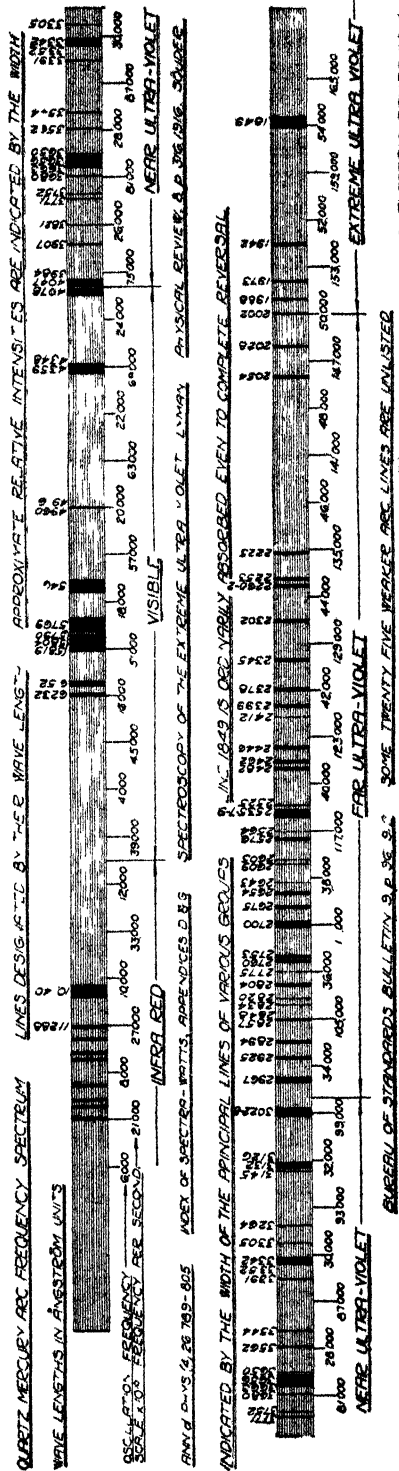


FIGURE 26. Quartz Mercury Arc Frequency Spectrum.

was standardized, iron was adopted as the positive electrode material, and an automatic starting device was introduced. Between 1907 and 1910, a commercial form of alternating current lamp was developed, and in the latter year a fluorescent reflector was put on the market. During the succeeding period a so-called orthochromatic lamp and a quartz mercury lamp were developed, and the problem of operating the alternating current lamp on a high power factor was solved.

Use as a Polariscopic Source. About the earliest use adopted by the chemist for the mercury arc was as a source of light for work with the polariscope and other optical instruments.⁵ At present, the tendency is to employ any usual laboratory quartz mercury arc for this purpose. Naumann⁶ finds the intense light of the modern mercury lamp to increase the accuracy of such work from two to three times.

Arcs started by tilting have the disadvantage of requiring a readjustment of the slit of any fine optical apparatus after having been put into operation. To avoid this, Harries and v. Hippel⁷ devised a bright, automatic starting arc which burns in any position. In a lamp possessing such an arc, a heating element produces a bubble of vapor which breaks a column of mercury in a capillary, thereby starting the arc. Such operation was based upon a lamp developed by Soltan⁸ but differed in having an extension vessel which permitted the arc to be operated in any position, as well as in having an automatic starting device. The use of a narrow tube and high pressure made the usual operating current of the lamp, run at 110 volts, only 150 milliamperes.

Since lines in the visible region are commonly employed in polarimetry, a quartz arc is not necessary. A compact glass lamp of high intensity, steady operation and suitable for many optical investigations has been described by Balinkin and Wells.⁹ It is a two-legged tube, the lower legs containing the mercury electrodes of unequal heights, the positive being the higher. A vertical tube above this serves as a condensing chamber. Constrictions in the lower limbs serve to retain mercury in the lower portions when the lamp is tilted for starting and so prevent the arc striking to the sealed in tungsten wires, overheating them, blackening the walls or cracking the seal. A ballast resistance is used to keep about one ampere at 35 volts across the terminals. Part of this resistance is cut out during the first half minute after the lamp has been started by tilting, so that for a brief period the newly formed arc carries three amperes.

Simple Arcs Developed in the Laboratory for Photochemical Studies. That the mercury arc might prove a valuable source for studying photochemical reactions in the ultraviolet were it enclosed in quartz soon became apparent. Such lamps were manufactured by Heraeus of Hanau in Germany as early as 1905 but, because of the expense of the quartz tubing, they remained laboratory curiosities for several years. As silica tubing became available, such lamps were used occasionally in a few laboratories. Recently, a number of workers have resumed investigations with laboratory-made quartz mercury arcs.

Among the first to employ a mercury arc as a source for effecting photochemical changes was Fischer,¹⁰ who used it in studies on the formation of ozone. He

⁵ Disch, J., *Ann. Phys.*, **12**, 1155 (1903); Schönrock, O., *Z. Verein. Deutsch. Zuckerind.*, **53**, 652 (1903); Lowry, T. M., *Trans. Faraday Soc.*, **7**, 267 (1912).

⁶ Naumann, H. N., *Biochem. Z.*, **229**, 269 (1930). The Osram high pressure mercury lamp is a satisfactory source for ultramicroscopy, according to K. Hoffmann, *Kolloid Z.*, **83**, 9 (1938).

⁷ Harries, W., and v. Hippel, A., *Physik. Z.*, **33**, 81 (1932).

⁸ Soltan, A., *Compt. rend. Pol. Phys.*, **4**, 301 (1929).

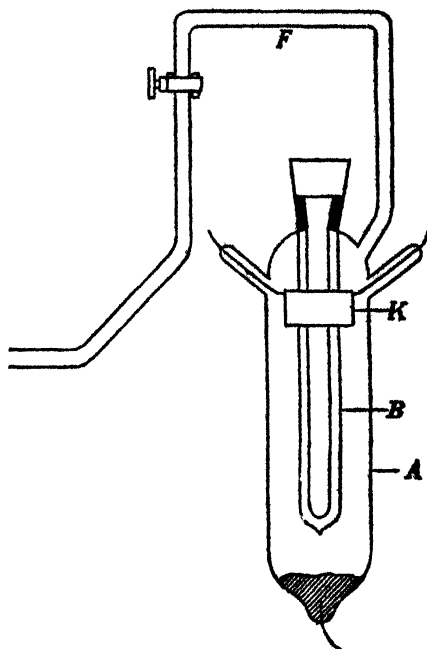
⁹ Balinkin, I. A., and Wells, D. A., *Rev. Sci. Instruments*, **3**, 388 (1932).

¹⁰ Fischer, F., *Ber.*, **38**, 2630 (1905).

fixed an exhausted double-walled quartz cylinder B (Figure 27) with sealing wax into the neck of a surrounding cylindrical glass vessel A, connected with an air pump by the tube F. The anode consisted of an iron ring K, surrounding the quartz cylinder and suspended by means of two platinum wires fused into the walls of the glass vessel. Mercury in the bottom of the latter served as cathode. The lamp was operated at 20 volts and 5 amperes, and was started by means of an induction coil. Arrangements were made to cool the lamp both internally and externally, so that the temperature in the interior of the lamp was kept down, thus maintaining a low density of the mercury vapor.

FIGURE 27.

Fisher's Lamp for Formation of Ozone.



Chapman, Chadwick and Ramsbottom¹¹ employed a similar principle in effecting gas reactions in a quartz bulb (Figure 28) enclosed in a glass mercury lamp in which the cathode was a pool of mercury and the anode a short cylinder of iron suspended in the upper part of the exhausted glass container. A somewhat more complex lamp, although very similar in principle, was used by Coehn and Becker¹² in their work on the oxidation of sulfur dioxide. (Figure 29.) The lamp consists of a glass vessel (4) in which the double-walled quartz vessel (2 and 3) is placed. A mercury seal is used at the top of the vessel (4). The lamp is located in the water-jacket or cooling vessel (5). To make the burning uniform a magnet (M) is placed in a glass tube in the lamp as shown. A quartz tube (1) is inserted in the vessel (2) through which gases may be passed by means of the inlet and outlet tubes (G).

Weigert¹³ bent the arc tube into a U-shape, and arranged the apparatus for

¹¹ Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, 91, 945 (1907).

¹² Coehn, A., and Becker, H., *Z. physik. Chem.*, 70, 90 (1910); *Z. Elektrochem.*, 13, 545 (1907).

¹³ Weigert, F., *Z. physik. Chem.*, 80, 67 (1912).

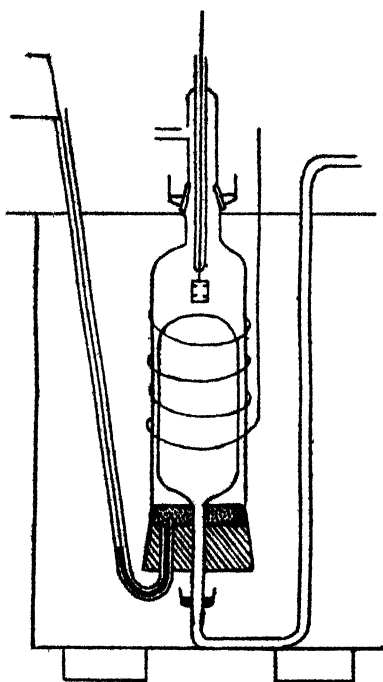
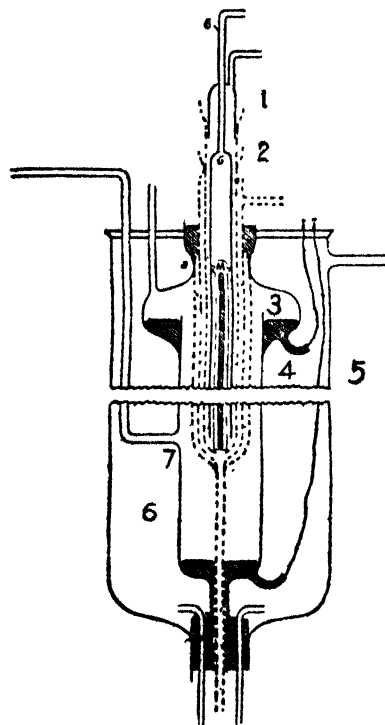


FIGURE 28.

Gas Irradiation Apparatus.

FIGURE 29.

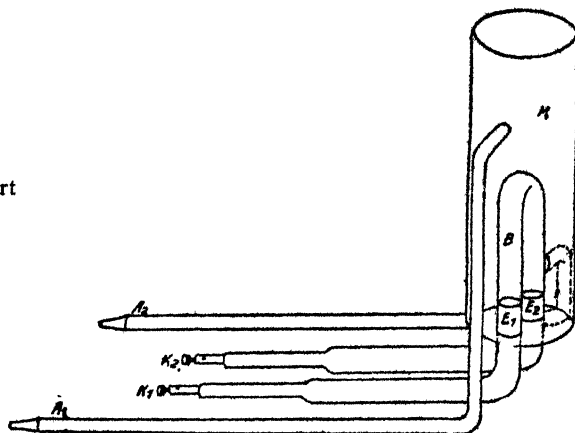


water cooling so as to avoid the effects of heat (from the lamp) on the reactions under investigation. He surrounded the lamp by the reacting gases, the vessel containing them being in turn immersed in the cooling water. (Figure 30.) A mercury arc was formed in the inverted U-tube B between surfaces of mercury E_1 and E_2 , electrical connection being made at K_1 and K_2 . The apparatus was mounted in a watertight casing having a quartz plate serving as a window if external exposures were to be made also.

Bovie¹⁴ constructed several lamps for biological experiments; these were not difficult to make and the design could be altered readily to suit particular requirements. Figure 31 shows a simple form based upon a lamp made by Kraus. A is

FIGURE 30.

Lamp Employed by Weigert
for Treatment of Gases.



a quartz tube one centimeter in diameter. One end is bent downward to form the positive electrode C. A quartz tube of the same diameter is sealed in, near the other end, to form the negative electrode B. The distance between B and C is about 10 cm. The end of the tube A forms a condenser. The lamp is sealed, after

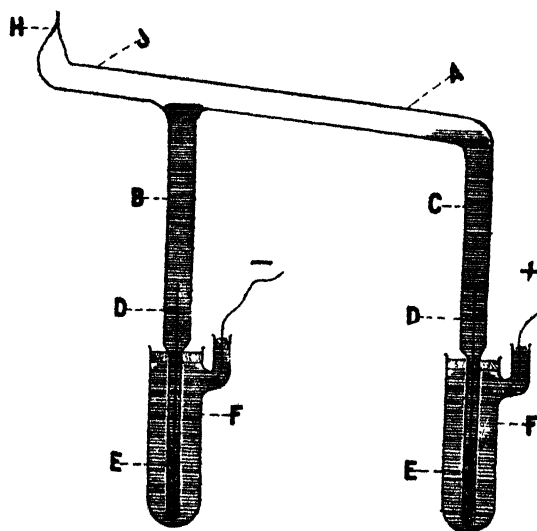


FIGURE 31.

Lamp Used by Bovie for
Biological Work.

exhaustion of gases at H. The tube A should be inclined to the horizontal position at an angle of 6° to 7° , the end (J) being higher, so that the condensed mercury

¹⁴ Bovie, W. T., *J. Biol. Chem.*, 20, 315 (1915).

will flow back into C. Pieces of five-millimeter quartz tubing are sealed to the lower ends of B and C. These in turn are set in mercury cisterns F,F (made of glass); test tubes may be used. The small tubes are sealed at E. The detail of the seal is shown in Figure 32. A bulb of wax on the outside is necessary in order to make the seal air-tight. The iron wire D conducts the electric current through the wax seal. The lamp should be used on a 110 volt direct-current circuit with five or six 16 c.p. bulbs in multiple as resistance, and will carry from 1.25 to 1.5 amperes, depending on the amount of cooling at the electrodes B and C.

Hulbert¹⁵ has described a simple laboratory lamp made of Pyrex or quartz, so designed that the seals for the electrodes and for the stopcock (through which the lamp is exhausted) can be made of wax. It will run normally for twenty hours or more before it requires re-exhausting. Another easily constructed lamp is due to Allen.¹⁶

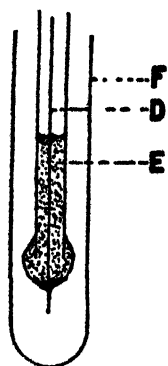


FIGURE 32.

Construction of Seal.

Arcs in glass with thin Pyrex windows, which were almost as efficient as quartz in transmitting ultraviolet, were described by Sonkin¹⁷ as inexpensive substitutes for the quartz mercury arc for spectrographic purposes. An apparatus for the production of radiations useful in accelerating the synthesis of formaldehyde from carbon monoxide and hydrogen has been proposed by Spindler.¹⁸ It involves the production of very hot arcs in mercury vapor at a pressure of several hundred kilograms, in a special steel furnace. Quartz or fluorite windows are provided.

THE DEVELOPMENT OF THE COMMERCIAL QUARTZ MERCURY ARC

Fundamental investigations of the operation of the mercury arc were early conducted by Küch and Retschinsky of the Heraeus firm at Hanau in Germany, about 1905 to 1907. Shortly after this, that firm manufactured a quartz mercury arc. The Cooper-Hewitt Co. began the manufacture of quartz lamps about 1910. During the early developmental period the problems to be solved concerned chiefly the nature of the electrodes and their function, the making of satisfactory seals for the electrical leads, the mechanism for starting the arc, the instability of the arc, and the relation of the pressure of the mercury vapor to the energy distribution and intensity of the radiations emitted.

¹⁵ Hulbert, E. O., *J. Opt. Soc. Am.*, 12, 519 (1926).

¹⁶ Allen, A. J., *Science*, 83, 336 (1936).

¹⁷ Sonkin, S., *J. Opt. Soc. Am.*, 19, 65 (1929).

¹⁸ Spindler, H., U. S. P. 1,880,333, October 4, 1932.

NATURE OF THE ELECTRODES

1. **Lamps With Both Electrodes of Mercury.** As the early arcs were a direct outgrowth of the carbon or iron arcs, it was usually felt necessary to have both of the electrodes pools of mercury. The arc was formed by so tilting the lamp as to make a mercury contact between the two pools and then in some manner breaking the column of mercury, the newly formed arc driving the mercury back into the pools in the electrode vessels.

Such lamps required elaborate temperature control by means of metal heat-radiating fans to maintain the proper distribution of mercury between the electrodes, or else it was necessary to introduce a suitable condensing chamber for the mercury. Bachmann¹⁹ claimed the elimination of this difficulty by using an anode of metal or alloy, the surface of which is amalgamated anew from time to time by means of mercury supplied from near the electrode.

Kent and Lacell²⁰ equalized the anode and cathode temperatures by bending the quartz tubes so that the electrodes were adjacent to each other. This was believed to prevent distillation of mercury from the hotter anode to the cathode, thereby extinguishing the arc. Belleaud and Barrolier²¹ used a heat conductor surrounding the electrodes to equalize their temperatures. They²² described a lamp to be immersed in a liquid to be sterilized, in which the cathode was screened from the liquid so that it was permitted to reach a temperature equilibrium with the anode. The mercury at the cathode automatically adjusted itself to a height favorable for operation depending upon the characteristics of the tube and the supply current.

There seem to be no direct early determinations to show whether the anode is, indeed, hotter than the cathode. In the lamp of Kelvin, Bottomley and Baird, it is the cathode which is cooled by aluminum radiating fans.

Von Recklinghausen²³ described elaborate methods for ensuring the proper distribution of mercury in lamps having a series of electrodes, now seldom employed.

To avoid the danger of breakage by mercury "slaps" during transportation of the lamp, von Türkenburg²⁴ filled the entire burner with mercury. During operation, mercury is displaced by the arc into a deformable anode receiver of rubber, provided with adequate cooling arrangements.

2. **Lamps with Anodes of Other Materials.** It soon became apparent that these difficulties might be avoided by using other materials for the anode. An iron anode was proposed by Fischer for the lamp previously described. Tian²⁵ made a lamp of a tube of transparent quartz through the center of which an insulated iron wire passed making contact with a drop of mercury (the cathode) at the bottom. The anode was a small iron cylinder. Ordinarily, direct current was used, but alternating current could be used if the anode was made double, *i.e.*, of two plates separated by a sheet of mica. This form of lamp had the advantage, besides low voltage operation, of being of a shape convenient for immersion in liquids. An

¹⁹ Bachmann, P., German P. 336,570, May 11, 1920; *J. Soc. Chem. Ind.*, **40**, 575A (1921).

²⁰ Kent, H. A., and Lacell, H. G., British P. 21,834 (1908).

²¹ Belleaud, R. L. M., and Barrolier, J., British P. 168,022, Dec. 10, 1920; 211,455, Jan. 25, 1924.

²² Belleaud, R. L. M., and Barrolier, J., U. S. P. 1,656,898, Jan. 24, 1928.

²³ von Recklinghausen, M., U. S. P. 1,091,244, March 24, 1914, and 1,110,574, Sept. 15, 1914.

²⁴ von Türkenburg, F. R., U. S. P. 1,896,651, Feb. 7, 1933.

²⁵ Tian, A., *Compt. rend.*, **156**, 1063 (1913).

early Cooper-Hewitt lamp²⁶ also employed iron as the positive electrode. Asada²⁷ used a brine-cooled steel anode which extended into the interior of the lamp and kept the temperature from getting too high, even when the lamp carried 20 amperes.

Carbon was employed for this purpose by Axmann²⁸ and by Kerschbaum,²⁹ the latter using nickel-steel pins to bring in the current. Perkin³⁰ mentioned the use of a tantalum button, in conjunction with mercury, for starting.

Because of its high melting point, tungsten was employed as anode by Urbain, Scal and Feige.³¹ It was then necessary to avoid even the smallest trace of oxygen or the walls of the enclosing vessel became darkened because of the production of volatile oxides. The use of tungsten was adopted in the lamps of George³² and of Nutting.³³

Sealed-in Leads. In order to produce vacuum-tight joints between the leading-in wires and quartz, Heraeus³⁴ proposed to use wires of iron or other metal having a temperature coefficient of expansion considerably greater than that of quartz. The diameter of the wire was to be such that the joint remained vacuum-tight at the highest anticipated temperature, the joint being reinforced by cements which melt at such a temperature. It was stated that an iron wire of 0.5 mm. diameter affords a vacuum-tight joint in quartz-glass at a dull red heat, and wires of 0.9 mm. diameter may be heated to 360°C. without the joint leaking.

Data on the expansion of fused quartz for temperatures up to 1000°C. were given by Holborn and Henning³⁵ who found that the mean increase of unit length for a rise of 1° is 0.00000054. Anderson³⁶ pointed out that Invar (an alloy with nearly the same coefficient of expansion as quartz) leads are unsatisfactory, since Invar melts below the fusing and working temperatures of quartz. Of other available metals, tungsten and molybdenum (coefficient of expansion 4.2×10^{-6}) are nearest to the thermal expansion of quartz, but molybdenum seals are only practicable in the case of very fine wires capable of carrying no more than one ampere. It was found that the tungsten seals which had been recommended by George could not be used. Lead or mercury seals had been described by the Thermal Syndicate. Anderson developed a method of working the quartz shell onto a core of a metal (tungsten, molybdenum, tantalum, platinum) of thermal expansion less than 9.0×10^{-6} and melting point higher than that of fused quartz (1750°C.), in which heat was applied to one end while the other was evacuated. The joint was tight at only one end; the slight space at the other was filled with a mixture of hydrocarbons. These must adhere³⁷ to both surfaces and not absorb water or gas, must have a low vapor pressure and change slowly in viscosity with temperature. A mixture of coal-tar pitch and residues of petroleum distillates, having a viscosity at 100°C. of 2000 dyne-seconds per square centimeter, was suggested.³⁸

²⁶ *Elektrotechnische Z.*, **26**, 941 (1905).

²⁷ Asada, T., *Proc. Phys.-Math. Soc. Japan* (3) **12**, 167 (1930); *Chem. Abs.*, **25**, 254 (1931).

²⁸ Axmann, *Elektrotechnische Z.*, **26**, 627, 1182 (1905).

²⁹ Kerschbaum, F., U. S. P. 1,118,868, Nov. 24, 1914.

³⁰ Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911).

³¹ Urbain, E., Scal, C., and Feige, A., *Compt. rend.*, **152**, 255 (1911).

³² George, H., U. S. P. 1,398,545, Nov. 29, 1921; *J. S. C. I.*, **41**, 49A (1922).

³³ Nutting, P. G., U. S. P. 1,320,087, Oct. 28, 1919, to Westinghouse Electric and Manufacturing Co.; *J. S. C. I.*, **39**, 8A (1920).

³⁴ Heraeus, German P. 336,014, Sept. 24, 1918; *J. Soc. Chem. Ind.*, **40**, 574A (1921).

³⁵ Holborn, L., and Henning, F., *Ann. Physik*, **10**, 446 (1903).

³⁶ Anderson, W. T., U. S. P. 1,909,797, May 16, 1933 (to Hanovia Co.).

³⁷ Anderson, W. T., U. S. P. 1,986,784, Jan. 8, 1935.

³⁸ See also British P. 356,056, Sept. 3, 1931, to Hanovia Co. for detailed discussion of a sealing arrangement. The use of rhodium coatings for the material to be sealed into quartz has recently been proposed by Harris, N. L., and Ryde, J. W., U. S. P. 2,113,984, April 12, 1938; British P. 477,462, Dec. 30, 1937; *Chem. Abs.*, **32**, 4299 (1938).

Lamps of the tungsten anode type may also be made by sealing the tungsten into glass, e.g., Nonex glass (coefficient of expansion, 3.9×10^{-6}), which is then united to the quartz tube by a graded seal, employing Pyrex (3.2×10^{-6}).³⁹ Keyes and Kraus⁴⁰ described new glasses available for making graded seals for this purpose. They contained various proportions of titanium and vanadium oxides, as well as boron oxide. Successive rings cut from tubes of these glasses were fused onto the silica tube. In the earlier lamps employing complicated seals, overheating of the seals had to be avoided by the use of metal radiating fins. A general discussion of such joints has been given by Buttolph.⁴¹ An ingenious method of sealing the annular ring guards at the anode and cathode of the silica tube so that they will be snug at the operating temperature of 400°C ., and still not crush the silica tube on cooling, has been described by him in a patent which must be consulted for details.⁴²

Methods of Starting the Discharge. Most quartz mercury arcs with either both electrodes or cathode only of mercury are started by tilting the lamp to form electrical contact by liquid mercury between the electrodes. Then, on again tilting the lamp back to its former position, the contact is broken and the arc is formed. Such a method was adopted in a water-cooled lamp of the Heraeus type used by Foster in 1906.⁴³

Parisi⁴⁴ describes a mercury arc enclosed in a two-by-five-inch quartz bulb, equipped with an Edison socket, for operation on an ordinary direct-current lighting circuit. The lead-in wires, equipped with special mercury seals, are connected through wire resistance coils separated by quartz slabs, to two half-inch pools of mercury in separate enlargements at the base of the lamp bulb. The lamp is started by tilting. The coils then become incandescent, heat the mercury vapor, or retard its condensation, and thereby add to the intensity of the ultraviolet emitted.

The design of certain proposed forms of the mercury arc lamp precluded the ordinary method of starting by tilting, and a number of ingenious, but relatively seldom employed, starting devices have been suggested. An electromagnet served to bring an iron anode into contact with the mercury cathode in one type of lamp developed by the General Electric Co. as well as in that devised by Hulburt.⁴⁵ In the lamp of Gallois,⁴⁶ mercury in the initial position fills the quartz illuminating tube. When the current is applied, a coil attracts an armature connected by a rod with the tube, and turns the latter on its axis about 40° , whereby, in consequence of the shape of the tube, the mercury is divided into two portions and an arc is formed across the intervening space.

At one time, Buttolph⁴⁷ proposed to seal the arc tube to the leads by the mercury itself, the ends of the arc tube being extended into mercury-filled boxes. By means of pistons, the mercury could then be forced into the tube to form a contact and start the arc.⁴⁸

Ulbrich⁴⁹ uses a wall to partly separate the anode mercury from the tube space:

³⁹ See also Goltstein, E., British Patent Application (void), 290,632.

⁴⁰ Keyes, F. G., and Kraus, C. A., U. S. P. 1,014,757.

⁴¹ Buttolph, L. J., *J. Opt. Soc. Am.*, 11, 549 (1925).

⁴² Buttolph, L. J., British P. 376,686, July 14, 1932.

⁴³ Foster, G. W. A., *J. Chem. Soc.*, 89, 913 (1906).

⁴⁴ Parisi, M., U. S. P. 1,954,888, April 17, 1934; 1,960,503, May 29, 1934 (to Goldberg, I.).

⁴⁵ Hulburt, E. O., U. S. P. 1,907,386, May 2, 1933.

⁴⁶ Gallois, J., *Bull. soc. encour. ind. nat.* 121.

⁴⁷ Buttolph, L. J., U. S. P. 1,831,998, Nov. 17, 1931.

⁴⁸ For special means of facilitating the starting of alternating current arcs, see Asada, T., *J. Inst. Elect. Eng., (Japan)*, 51, 51 (1931); Steinmann, A., British P. 356,355, Sept. 10, 1931; Matouch, R., U. S. P. 1,750,482; Sperti, G., U. S. P. 1,889,079, Nov. 29, 1932.

⁴⁹ Ulbrich, W., U. S. P. 1,694,836, Dec. 11, 1928.

from the wall, one or more fine tubes extend the length of the tube, but are located outside of the luminous band. On tilting the lamp, mercury passes through the fine openings, so that it reaches the cathode from the end of the tube in a fine stream or streams. The use of the latter in starting avoids a sudden onrush of mercury, which might extinguish the newly formed arc, on restoring the arc to its normal position.

The lamp of Kent and Lacell⁵⁰ was started by electrically heating a small coil of wire placed around the arc tube. When started, the current was automatically cut off from the heating wire. This lamp, which was not evacuated, was burned on a 500 to 1000 volt circuit, and was extremely powerful. Preheating coils, which vaporize some of the mercury in about a minute to form contact with the anode and start the arc, have been used in various lamps. Their use also shortens the build-up period during which a steady ultraviolet intensity becomes established. A number of patents describe such devices.⁵¹

Electrical Starting Devices. For large-scale installations, for arcs of peculiar design to meet special irradiation conditions, and particularly for the long, low-pressure Cooper-Hewitt illuminating apparatus, the arc is usually formed by special auxiliary electrical equipment. In each instance there are involved, according to Buttolph,⁵² who has reviewed the subject in detail, both the formation and maintenance of a hot spot on the cathode surface and the coincident ionization of mercury vapor between the electrodes.

With some types of arcs, the initial resistance was overcome by the aid of an induction coil, but this is usually impractical for large industrial arcs. In certain cases, however, in which the cathode spot has been formed and maintained by a small local arc to an auxiliary anode, or in which independently heated Wehnelt cathodes (see Chapter 8) are used, ionization of the vapor through the arc tube may be brought about by small Ruhmkorff coils of the kind commonly used as leak testers in high vacuum work with glass apparatus.

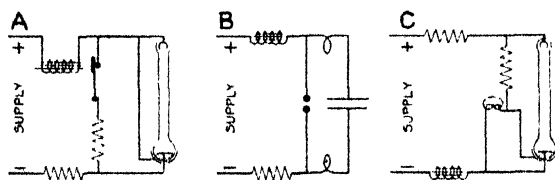


FIGURE 33. Circuits for Starting Mercury Arcs (Buttolph and Dana, *Review Scientific Instruments*).

Buttolph and Dana⁵³ state that the use of the operating reactance as a source of induced high voltage for arc starting (Figure 33, A) was described in patents applied for by Peter Cooper-Hewitt in 1900 to 1902. At this time the "inductance coil" was generally placed in the circuit adjacent to the arc anode, with an electrolytic interrupter or magnetically operated coil switch in multiple with the arc tube. Resistance in series with the interrupter switch kept the current sufficiently low so that it could

⁵⁰ Kent, H. A., and Lacell, H. G., British P. 21,834 (1908); Perkin, F. M., *Trans. Faraday Soc.*, 6, 199 (1911).

⁵¹ Thompson, A., U. S. P. 1,962,106, June 5, 1934; Hulett, M., U. S. P. 1,886,400, Nov. 8, 1932; Blake, G. J., and Leadbetter, G., British P. 294,288, July 23, 1928.

⁵² Buttolph, L. J., *Rev. Sci. Instruments*, 1, 498 (1930).

⁵³ Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, 4, 206 (1933).

be handled by the switch. The inductance of the lead wires, the capacity of the arc tube and the switch arc as indicated in the functional diagram B, constitute an elementary oscillatory circuit receiving its energy from the inductance coil. Such a circuit has a very high frequency and low efficiency. The effectiveness of the circuit depends upon the effectiveness of the interrupter switch, called a shifter. A high capacity mercury interrupter,⁵⁴ originally devised by Hewitt to take the place of the generally used spark-gaps in high-frequency generators, was adapted by Thomas⁵⁵ for use as a shifter switch in a starting circuit schematically shown in diagram C. When the apparatus is connected with the supply line, current flows through the auxiliary circuit, and the magnetic field of the inductance rotates the shifter switch forming a transient unstable arc in it. The resistance in series with the shifter is of an amount which makes the current too small to maintain the cathode hot spot. Furthermore, the stability of the shifter arc is decreased by the condenser between the mercury in the main arc and a tin-foil coating on the outside of the mercury chamber. When, after about 0.05 second, the arc is extinguished, the energy of the inductance is delivered as a single steep polarized wave-front impulse which tends to induce a negative potential of several thousand volts on the mercury cathode of the main arc. From an irregularity in the surface of the mercury formed by a coating of carborundum crystals fused into the glass, a localized discharge passes into the gas space and starts the main arc.⁵⁶

Inert gases are also used in starting arcs. At first they were employed to strike the arc by breaking the mercury column when pumped into the lamp by some suitable arrangement.

In general, however, they serve as conductors through the discharge space until enough mercury has been vaporized to carry the arc. Bayle, Fabre and George⁵⁷ found that a direct-current, quartz mercury lamp containing argon at a pressure of 500 mm. of mercury, strikes instantaneously on application of the voltage and relights automatically if the arc should happen to be extinguished. Geffcken and Richter⁵⁸ believed argon the most suitable noble gas to use for this purpose. (See also Chapter 8.)

The Pressure of the Mercury Vapor. Various methods for improving the vacuum⁵⁹ or for exhausting the lamp space have been described.⁶⁰ During the earlier development of the Cooper-Hewitt and other commercial arcs, it was generally believed that to produce a stable arc, a low pressure of mercury vapor is essential. Kent and Lacell,⁶¹ however, recognized that increased pressure is not the cause of the instability of the arc. Evidence in favor of the use of a higher mercury vapor pressure was afforded by Henri⁶² in experiments which demonstrated that the ultraviolet radiation from a mercury vapor lamp becomes more intense as the tem-

⁵⁴ Pierce, G. W., *Proc. Am. Acad. Sci.*, **39**, 389 (1904).

⁵⁵ Thomas, P. H., U. S. P. 1,079,380 (1906).

⁵⁶ For details of means for securing mercury surfaces effective for starting, see patents of Winninghoff, W. J., U. S. P. 1,831,985-6 (1931) and 1,971,945, Aug. 28, 1934; British P. 288,737, April 19, 1928. Another description of an electrical starting mechanism is given by the Schering-Kahlbaum, A.-G., British P. 364,356 and 364,393.

⁵⁷ Bayle, E., Fabre, R., and George, H., *Bull. Soc. Chim.*, **37**, 89 (1925); *Rev. d'optique*, **1** (1925).

⁵⁸ Geffcken, H., and Richter, H., British Patent Application (void), 267,127. See for a limitation of the proportion of rare gas, N. V. Phillips' Gloeilampenfabrieken, British P. 474,192, Oct. 27, 1937; *Chem. Abs.*, **32**, 2854 (1938).

⁵⁹ von Recklinghausen, M., U. S. P. 1,110,576, Sept. 15, 1914; Thompson, W. P., British P. 28,757, Dec. 20, 1911; *Chem. Abs.*, **7**, 1846 (1913); Helbronner, A., and von Recklinghausen, M., British P. 14,129, June 10, 1910.

⁶⁰ Bowie, W. T., *J. Am. Chem. Soc.*, **37**, 1721 (1915); Waran, H. P., *J. Sci. Instruments*, **1**, 54 (1923).

⁶¹ Kent, H., and Lacell, H., British P. 21,834 (1908).

⁶² Henri, V., *Compt. rend.*, **153**, 426 (1911).

perature of the luminous tube is allowed to rise. By cooling the tube with water, the radiation was found to be fourteen times less powerful than with air-cooling, the same number of watts being consumed. A number of lamps were introduced in which the mercury vapor pressure was atmospheric or greater. These included the Cornu type lamps, the Kelvin, Bottomley and Baird lamp and others.⁶³ Bernhardt⁶⁴ built a mercury lamp which burned in carbon dioxide of up to 650 atmospheres pressure and carrying 400 amperes.

The U-shaped lamps of which mention has been made probably owed their greater relative output of ultraviolet rays to a higher vapor pressure of mercury due to a lessening of the cooling of the adjacent mercury electrodes rather than, as had been thought, to an altered distribution of mercury. The bent tubes of such lamps, however, tended to deteriorate or become opaque since the arc in making the bend

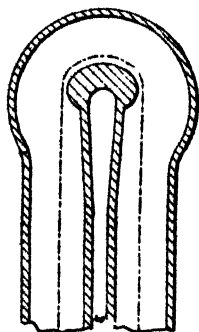


FIGURE 34.

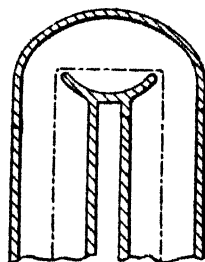


FIGURE 35

does not follow the shape of the tube. Instead, as indicated by the dotted line of Figure 34, it tended to approach the side of the curved portion of the tube nearest the center of curvature, subjecting it to an extremely high temperature. To counteract such destructive action, this portion of the tube was made of increased thickness or projections (Figure 35) were added to divert the arc stream.⁶⁵ Von Recklinghausen⁶⁶ also described methods of prolonging the life of his lamps by lining the portion near the hot cathode spot with a highly refractory material such as "titanium zircon quartz."

COMMERCIAL MERCURY-VAPOR ARCS (MERCURY CATHODE TYPE)

Modern commercial mercury-vapor lamps with mercury cathodes are of two main types, those having a mercury anode and those having an anode of tungsten or other metal. The first is built along the lines of the Heraeus lamp. The Hanovia quartz mercury⁶⁷ arc lamp, Figure 36, consists essentially of three parts, the tube through which the arc plays, the anode vessel and the cathode vessel. The current is carried to the lamp through nickel rods ground into the side tubes of the electrode

⁶³ U. S. P. 1,343,037; British P. 129,022 and 129,702; *J. Soc. Chem. Ind.*, 622A (1919); Berlemon, G., *Bull. soc. encour. ind. nat.*, 133, 254 (1921); *Chem. Abs.*, 15, 2163 (1921); Stammreich, H., *Naturwiss.*, 12, 744 (1926).

⁶⁴ Bernhardt, F., *Physik. Z.*, 27, 713 (1926).

⁶⁵ von Recklinghausen, M., Helbronner, A., and Henri, V., U. S. P. 1,176,481, Aug. 29, 1916; 1,271,246, July 2, 1918.

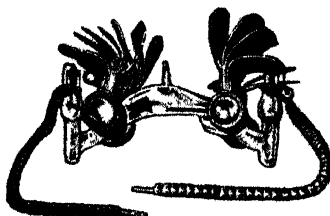
⁶⁶ von Recklinghausen, M., U. S. P. 1,188,587, June 27, 1916.

⁶⁷ Hanovia Chemical and Manufacturing Co. (A more recent type is discussed in Chapter 8.)

vessels. The ground-in joints are sealed with mercury. Small quartz tubes are used in the electrode vessels to avoid "hammering" of the mercury. The lighting of the lamp is effected by turning the lever slowly around from position to position so that a stream of mercury flows from anode to cathode, making a short circuit between the two poles. On breaking the stream, the arc is struck, and the level must be brought to its original position to allow the mercury to flow back into the

FIGURE 36.

Hanovia Lamp for Direct Current.



Courtesy Hanovia Chemical and Manufacturing Co.)

anode vessel. After lighting, the lamp may be turned again by the lever into a vertical position in which it can be continuously used. The arc may be used end-on in a horizontal position by viewing it from the anode end, or in a vertical position from above. On 220-volt lines the lamp may be burned at all potentials between the electrodes from 25-185 volts by means of a variable resistance of 55 to 95 ohms (depending on the type of lamp) connected in series; on 110-volt lines at all potentials from 25-80 volts by means of a variable resistance of 25 or 40 ohms. If the lamp is not required to burn at low voltages, resistances of 30 or 50 ohms and of 12 or 20 ohms suffice. At low potentials the arc or electric discharge fills the whole cross-section of the tube. With increasing potential, the cross-section of the arc diminishes more and more, and forms eventually a thread of some five millimeters diameter. The specific intensity of the visible and ultraviolet radiation is the same, and the economy equally as good in 110-volt as in 220-volt lamps. With constant external conditions the light exhibits a desirable degree of constancy. The Hanovia vapor lamp is also made for operation on alternating current, the difference in construction being that for this current it is necessary that there be two positive electrodes in place of the one ordinarily used for direct current.

Problems concerned with the design of pole vessels and the use of constrictions between these and the luminous tube to prevent alterations in the distribution of mercury during operation, have been studied by the Hanau firm.⁶⁸ By the use of a capillary at the anode, it is claimed that both vessels may be made of the same size and shape, and both may be completely filled with mercury. With alternating currents, two anode vessels have condensing chambers and separate connections by tubes with the luminous portion are necessary.

Anderson and Fraser⁶⁹ stated that in such lamps the proper temperature is usually maintained by radiation from metallic fins. If the lamp became too hot and the vapor pressure too high, the current would drop to values insufficient to maintain the cathode hot spot (which they believed to have a temperature of 2270°C.) and the arc would be extinguished. To avoid the necessity of using large volumes of mercury they proposed to immerse non-amalgamating metals of higher thermal conductivity such as wires, rods, meshes, tubes or plates of tungsten or molybdenum

⁶⁸ British P. 286,317, May 9, 1929.

⁶⁹ Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932, to Hanovia Co.

in the mercury in contact with the walls. Anderson⁷⁰ described methods of reducing the size of the container to one-half or one-third its previous size.

Water-cooled lamps are usually U-shaped, as in the case of those developed by Kent and Lacell. Bird⁷¹ designed a burner in which the effects of expansion of liquid mercury upon the positions of the two mercury levels were minimized. By dividing the anode pool by inserting a smaller tube within the anode tube, it was possible to lessen the effect of the temperature of the pool upon the vapor pressure of the arc. The small inner portion at a high temperature served as the terminal for the arc stream and the other, at a reduced temperature, acted as a receiver for the vaporized mercury. The cathode pool was believed to exert a smaller influence upon the vapor pressure than the anode pool. The area of the cathode pool was made great by means of a bulb in order to lengthen the thermal path from the arc stream to the wall.

The "hot anode" type of quartz mercury vapor lamp, known as the "Uviarc," has no mercury chamber at the anode end.⁷² In place of mercury, a tungsten target composed of a spiral formed of tungsten wire is used. The anode end is protected from mechanical injury by means of a metal cap which also serves to lead the current to the anode. The cathode end is reinforced with thick quartz to absorb the shock of the mercury vapor and is set at an angle which is claimed to reflect back into the luminous portion of the tube some ultraviolet rays which would otherwise escape. The cathode end is also protected by a metal cap through which the current is led to the mercury. The tungsten wire, serving to lead the current into the lamp, is sealed into the quartz tube by a graduated mixture of quartz and glass so that at the end there is practically pure glass, while the portion next to the quartz tube is practically pure quartz. It is claimed that this combination of glass and quartz provides a proper coefficient of expansion so that the loss of vacuum is prevented. Having only one mercury electrode, this lamp is capable of being operated in either a vertical or horizontal position, which in certain cases is of advantage. A slightly different design is employed when tungsten anode ("Uviarc") lamps are intended to be run generally in a vertical or nearly vertical position. The change is principally in the construction of the cathode chamber. The Uviarc is a direct current device. It may itself function as a rectifier.⁷³ An alternating current Uviarc with double anode is made for certain applications.

The development of Cooper-Hewitt lamps has followed two distinct courses for visible and for ultraviolet output. The original mercury arc has been developed as a long low pressure arc for illumination of industrial establishments. LeBlanc⁷⁴ gave an early account of the construction, current consumption and efficiency of such lamps. Details of the more recent developments are to be found in the various articles of L. J. Buttolph cited in this chapter.

Our present concern is not, however, with the low-pressure illuminating arc, but rather with the high-pressure quartz arc just described. A small high intensity arc ("Labarc"), operating on 110 volts, either alternating or direct current, was described by Buttolph⁷⁵ in 1922. In it the effective light zone was one-quarter by one and three-quarter inches. It was especially suited for employment with filters, as a monochromatic light source. It was then shown that by introducing suitable

⁷⁰ Anderson, W. T., Jr., U. S. P. 1,902,936, March 28, 1933, to Hanovia Co.

⁷¹ Bird, L. F., U. S. P. 1,952,306, March 27, 1934, to Hanovia Co.

⁷² Cooper-Hewitt Electric Co., now General Electric Vapor Lamp Co.

⁷³ Buttolph, L. J., *Gen. Electric Rev.*, 13, 741 (1920).

⁷⁴ LeBlanc, M., *Electrical Rev. and Western Electrician*, 57, 1248 (1910).

⁷⁵ Buttolph, L. J., *J. Opt. Soc. Am.*, 6, 1066 (1922).

resistance in series with the lamp it would function as a low-pressure arc giving only the strongest spectral lines. A detailed discussion of the operating conditions of the Uviarc is given in a following section.

A number of recent patents have been concerned with lamps, developed for specific purposes and with accessories as cabinets, etc. Burners enclosed in hoods may be prevented from overheating by sucking the hot air away by an electric fan attached to the upper part of the hood. According to Cooper,⁷⁶ this results in a saving of power. A cabinet for an arc for home use in therapy has been described by Link,⁷⁷ and a prepayment "coin-in-the-slot" time-switch control has been devised⁷⁸ for installations of the mercury arc in bath houses, therapeutic institutes and beauty parlors.

Therapy lamps adapted for introduction into various body cavities have been described by Philip.⁷⁹ They embody small U-tubes carrying the mercury arc, surrounded by a long, narrow quartz envelope with cooling water or gas. A number of other therapy arcs, not, however, adapted for introduction into orifices, designed by Nisbet⁸⁰ involved modifications of structural detail and new combinations of previously described principles.

To avoid the deposition of mercury on the luminescent part of a lamp intended to be submerged in water during use, Gourdon⁸¹ located it in an evacuated vessel, the nipple of the luminescent part of the lamp passing through the wall of the vessel near the nipple of the vessel itself. This lamp was intended to be put to such curious uses as catching fish, maturing oysters and illuminating submarine operations.

An assembly of base, pedestal, hood with lips, and applicators suitable for ultraviolet therapy, has been patented by Chesney and MacLagan.⁸² The Hanau firm⁸³ described a handle by which a therapy lamp could be carried about without danger of altering the distribution of the mercury.

THE THEORY OF THE OPERATION OF THE MERCURY ARC

A. Electrical Conduction Processes. The general theory of the processes occurring in the arc has been treated in the previous chapter; this section deals with those processes which are especially characteristic of the arc in which the predominant conduction is by a mercury cathode and by mercury vapor in the space between the electrodes. Comparatively few investigations have been devoted to the nature of the manner in which the anode functions even in the case of the lamps of the Hanovia type in which the anode is mercury. As noted elsewhere, Compton⁸⁴ has stated that the entire problem is concentrated at the cathode, as other processes, especially those in the plasma, have been essentially explained by the work of Langmuir and Mott-Smith,⁸⁵ Tonks and Langmuir,⁸⁶ Eckart and Compton,⁸⁷ and Killian.⁸⁸

1. *The Conduction of Current from the Cathode.* It was at first believed that the current was carried by electrons thermionically emitted from the cathode,⁸⁹ the temperature of which was then assumed to be about 2500°K. This had to be rejected when subsequent work showed that the cathode could not be hotter than

⁷⁶ Cooper, C. A., British P. 305,758, February 14, 1929.

⁷⁷ Link, D. C., U. S. P. 1,668,566, May 8, 1928.

⁷⁸ Bar, N., v. Recsey, N., and v. Recsey, E., British P. 382,349, October 27, 1932.

⁷⁹ Philip, G., British Patent Application (void), 298,903, October 15, 1928.

⁸⁰ Nisbet, J., British P. 248,796, March 11, 1926.

⁸¹ Gourdon, G., British P. 390,108, March 30, 1933.

⁸² Chesney, J., and MacLagan, H. P., U. S. P. 1,813,383, July 7, 1931, to McIntosh Electrical Corp.

⁸³ British P. 286,318, June 4, 1929.

⁸⁴ Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931).

⁸⁵ Langmuir, I., and Mott-Smith, H., *Gen. Electric Rev.*, **27**, 449, 538, 616, 762, 810 (1924).

⁸⁶ Tonks, L., and Langmuir, I., *Phys. Rev.*, **34**, 876 (1929).

⁸⁷ Eckart, C. H., and Compton, K. T., *Phys. Rev.*, **24**, 97 (1924).

⁸⁸ Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).

⁸⁹ Stark, J., *Ann. Physik*, **12**, 673 (1903).

600°-800°.⁹⁰ Later calculations by Compton⁹¹ indicate the surface temperature of the cathode spot not to exceed 200°C.

Earlier observers, as Güntherschulze,⁹² gave large values for the rate of vaporization of mercury from the cathode, *e.g.*, 7.2×10^{-8} gram per ampere per second. The suggestion of Compton and van Voorhis that this was in part due to mechanical loss as spray was verified by von Issendorff, who found a corrected rate of less than $0.3\text{--}1.3 \times 10^{-8}$ gram per ampere per second. Kobel⁹³ placed it at only 0.017×10^{-8} and Nikiforov⁹⁴ places it at only 0.4 milligram per ampere per second. This indicates but a minute loss at the cathode. These new data show that the vapor pressures at the cathode spot must be considerably less than the atmosphere or more assumed in the earlier literature.

Slepian⁹⁵ suggested that the current might be carried by positive ions arising from thermal ionization of the vapor just outside the cathode; Compton, however, objected that this theory failed to suggest a mechanism for the input of energy into the assumed high temperature region. The currently accepted theory is that of Langmuir⁹⁶ of "field currents" due to a strong field concentrated at the cathode region. The minimum value of the field was calculated by Lamar and Compton⁹⁷ to be at least 7.6×10^4 volts per centimeter. Mackeown, assuming 5 per cent of the current to be carried by positive ions, calculates it to be 5×10^5 volts per centimeter. If 1.3×10^6 volts per centimeter be assumed necessary to give the observed cathode current density of 4000 amperes per square centimeter,⁹⁸ the cathode drop will occur within a distance of 10^{-5} centimeter. Lamar and Compton consider it to occur within a space of less than 1.76×10^{-4} centimeter, and give the cathode potential drop as about 10 volts (9.9 volts).⁹⁹ An earlier value of only 5.27 volts¹⁰⁰ was said to have been based upon the use of an erroneous probe method. Killian¹⁰¹ also found about 10 volts and Gaudenzi¹⁰² about 9 volts. Kommnick and Lübcke¹⁰³ find quite similar values, so that the mercury arc must be regarded as a special case of a low voltage arc. It was even found possible by Hebb¹⁰⁴ to maintain an arc in mercury vapor at only 1.7 to 1.8 volts although the 2537 line requires for its excitation (see below) 4.9 volts. Such an abnormal arc has been studied by Bär,¹⁰⁵ whose arc burned at 3.5 volts at 175°C. Unlike the earlier abnormal arcs, this was not due to oscillations, but to some positive space charge maintained before the cathode. Reverse fields sometimes play a part.¹⁰⁶

After discussing in detail the attempts to determine from heat balance data the

⁹⁰ Mason, R. C., *Phys. Rev.*, **38**, 427 (1931); Compton, K. T., and van Voorhis, C. C., *Proc. Nat. Acad. Sci.*, **13**, 336 (1927); Compton, K. T., *Trans. Am. Inst. Elec. Eng.*, **46**, 868 (1927); Seeliger, R., *Physik. Z.*, **27**, 37 (1926); Lübcke, E., *Z. tech. Physik*, **10**, 598 (1929).

⁹¹ Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931).

⁹² Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

⁹³ Kobel, E., *Phys. Rev.*, **36**, 1636 (1930).

⁹⁴ Nikiforov, A. Y., *J. Exptl. Theoret. Phys. (U.S.S.R.)*, **6**, 168 (1936); *Chem. Abs.*, **31**, 14 (1937).

⁹⁵ Slepian, J., *Phys. Rev.*, **27**, 407 (1926).

⁹⁶ Langmuir, I., *Science*, **58**, 290 (1923); *Gen. Electric Rev.*, **26**, 735 (1923); see also Mackeown, S. S., *Phys. Rev.*, **34**, 611 (1929).

⁹⁷ Lamar, E. S., and Compton, K. T., *Phys. Rev.*, **37**, 1069 (1931); see also Gvosdover, S. D., *Physik. Z. Sowj.*, **7**, 274 (1935).

⁹⁸ Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

⁹⁹ Lamar, E. S., and Compton, K. T., *Phys. Rev.*, **37**, 1069 (1931).

¹⁰⁰ Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann. Physik*, **18**, 213 (1905).

¹⁰¹ Killian, T. J., *Phys. Rev.*, **31**, 1122 (1928).

¹⁰² Gaudenzi, A., *Brown-Boveri Rev.*, **16**, 303 (1929).

¹⁰³ Kommnick, J., and Lübcke, E., *Physik. Z.*, **33**, 215 (1932).

¹⁰⁴ Hebb, T. C., *Phys. Rev.*, **16**, 375 (1920), see also Yao, Y. T., *Phys. Rev.*, **21**, 1 (1924).

¹⁰⁵ Bär, R., *Z. Physik*, **31**, 430 (1925).

¹⁰⁶ Rudy, R., *J. Frank Inst.*, **201**, 248 (1926); v. Dziewulski, H., *Z. Physik*, **69**, 366 (1931).

fraction of the current carried by electrons and by positive ions at the cathode, Compton¹⁰⁷ concluded these to be futile since the range of certain quantities needed in the calculations was not known. It was, however, possible to show that the heat balance may be made consistent with Langmuir's theory and with the known facts of ionization by making certain reasonable assumptions regarding the unknown fraction of energy returned to the cathode by unelectrified carriers such as neutral atoms in various energy states, or by radiation.

The cathode spot moves rapidly on the mercury surface as it becomes conditioned and migrates to a neighboring spot where the mercury surface is contaminated by impurities and where the electrons can be more readily extracted. The mercury surface becomes depressed and the electrons probably come from the irregular edge of the crater, which is then immediately depressed, due to the vapor pressure of the mercury, heated by the bombardment of positive ions at the cathode spot. This would also account for the rapid movement of the cathode spot, since the electrons always come from the edge of the crater, which is then depressed by the increased vapor pressure at that point. Tonks¹⁰⁸ described methods of preventing this unsteadiness at the cathode end of the positive column by the use of wires of certain metals, especially molybdenum, the cathode spot being limited to the line of wetting. From the spectral distribution of the radiations from such anchors, it was suggested that there might be a region of "hot" ionized gas close to the cathode. Cravath¹⁰⁹ studied the behavior of the mercury vapor arc with a jet of liquid mercury as cathode, but was unable to obtain a stationary cathode spot on the jet.

It has been found that the mercury arc can be operated with the cathode frozen at -70°C , the voltage being not much higher than that for the normal operation of the arc.¹¹⁰ Newman¹¹¹ has also studied the operation of the mercury arc at liquid air temperatures, his experiments supporting the idea that the fraction of the current carried by electrons depends on the vapor pressure. The parts of the arc immersed in liquid air were not luminous, but there was a brilliant cathode spot.

2. *Conduction Processes in the Plasma.* Little need be added here to the general discussion of this topic given in the previous chapter. As in general in the gaseous discharge, the tension, U , on the electrodes of a mercury arc is a linear function of the arc length l , i.e., $U = A + Bl$, in which A is the sum of the anode and cathode drops of potential and B is the voltage gradient in the arc. Pawlikowski¹¹² found the mean velocity of all electrons to be constant throughout the whole width of the positive column, although in the immediate vicinity of the cathode two groups of electron velocities were noted.

The theory of the striated glow discharge in mercury vapor was studied by Compton, Turner and McCurdy.¹¹³ In this work, attention was drawn to the importance of cumulative ionization in the striations. This concept has since been extended to the phenomena in the ordinary discharge.

There have been many divergent statements in regard to the transfer of mercury

¹⁰⁷ Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); Compton, K. T., and Langmuir, I., *Rev. Modern Physics*, **2**, 184 (1930). For other earlier attempts, see Güntherschulze, A., *Z. Physik*, **31**, 509 (1925); Seeliger, R., *Physik. Z.*, **27**, 22 (1927); *Elektrotech. Z.*, **49**, 853 (1927); Compton, K. T., and van Voorhis, C., *Proc. Nat. Acad. Sci.*, **13**, 336 (1927); v. Issendorf, J., *Physik. Z.*, **29**, 857 (1928). See also Gehrts, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932), and Weizel, W., Rompe, R., and Schon, M., *Z. Physik*, **112**, 339 (1939).

¹⁰⁸ Tonks, L., *Physics*, **6**, 294 (1935).

¹⁰⁹ Cravath, A. M., *Phys. Rev.*, **36**, 1480 (1930).

¹¹⁰ Kawa, J., *Acta. Phys. Polonica*, **1**, 427 (1932); *Chem. Abs.*, **28**, 4667 (1934).

¹¹¹ Newman, F. H., *Phil. Mag.*, **18**, 607 (1934).

¹¹² Pawlikowski, J., *Acta. Phys. Polonica*, **2**, 59 (1933); *Chem. Abs.*, **28**, 7155 (1934).

¹¹³ Compton, K. T., Turner, L. A., and McCurdy, W. H., *Phys. Rev.*, **24**, 597 (1924).

between the electrodes of the direct-current arc. Perot,¹¹⁴ who made one observation of the change in mercury levels in an inverted U-arc, believed all of the current to have been carried by univalent mercury ions. Matthies,¹¹⁵ however, found no mercury transfer other than that due to thermal processes and believed the conduction to be entirely electronic. Other workers took intermediate positions. Güntherschulze¹¹⁶ believed half of the current carried by electrons and half by ions and Schottky and von Issendorff,¹¹⁷ that 80 per cent was carried by ions. The more recent calculations of Langmuir have shown that the positive ion current is not more than 1/340 to 1/605 of the electron current density. Tonks¹¹⁸ states that of the current carried by mercury ions 50 per cent is by doubly and 12 per cent by triply charged ones.

Forbes and Leighton,¹¹⁹ using a lamp which was too hot to allow condensation of mercury to occur on the walls, found the ratio between the gram atoms of mercury transferred from the anode to the cathode and the faradays passing through the lamp to be sensitive to cathodic cooling and that mercury can migrate against considerable temperature gradients. Extrapolation of their results to the lowest voltage gradients and pressures indicated a minimal mercury transfer and an insignificant role for the positive ions. But, as the voltage gradient and the pressure rise, the positive ion current appears to gain on the electron current. At five volts per centimeter, the ratio has reached five, almost irrespective of the current, and remains near that value up to 25 volts per centimeter and a pressure of three atmospheres. Elenbaas¹²⁰ has discussed the theory of the gradient of the high-pressure mercury discharge.

3. *The Pressure in the Arc.* Küch and Retschinsky¹²¹ measured over twenty internal pressures in an arc 12 mm. in diameter. Between 3 and 18 volts per centimeter, the pressure rose from 38 to 1500 mm., the current varying between 4.1 and 5.05 amperes; they gave, however, no quantitative correlation between the pressure and other variables.

Forbes and Leighton,¹²² realizing that the electrical conditions depend on the resistance, pressure and the efficiency of air and water-cooling, presented graphs relating the pressure to the voltage gradient for arcs of 9 and 2 mm. diameter, (see Section on Constricted Arcs, Chapter 6) each carrying various currents. They concluded

(a) The pressure is a function of the cross section, voltage gradient and current, but not of the arc length or the relative cathode and anode temperatures.

(b) In spite of wide differences in the arc cross section and the current carried, the pressure changed about 140 mm. for a unit change in the voltage gradient, and the curves became nearly parallel at pressures greater than two atmospheres.

(c) For a given lamp at constant voltage, the pressure is very roughly proportional to the logarithm of the current.

(d) At low voltage gradients, the ratio of pressure to cross section for a given current strength is nearly the same for the constricted arc as for the normal arc, but at higher voltage gradients, the ratio is greater for the constricted arc.

¹¹⁴ Perot, A., *J. Phys.* (5), 1, 609 (1911).

¹¹⁵ Matthies, W., *Ann. Physik*, 37, 721 (1912).

¹¹⁶ Güntherschulze, A., *Z. Physik*, 11, 75 (1922); 31, 509 (1925).

¹¹⁷ Schottky, W., and von Issendorff, J., *Z. Physik*, 26, 85 (1924).

¹¹⁸ Tonks, L., *Elec. Eng.*, 53, 239 (1934).

¹¹⁹ Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, 12, 53 (1926). For the clean-up of mercury by the walls, Kenty, C., *J. Applied Phys.*, 9, 765 (1938).

¹²⁰ Elenbaas, W., *Physica*, 1, 673 (1934), 2, 757, 767, 787, 807 (1935); 4, 279 (1937); *Phys. Rev.*, 55, 294 (1939).

¹²¹ Küch, R., and Retschinsky, T., *Ann. Physik*, 20, 563 (1906).

¹²² Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, 12, 53 (1926).

(e) Had there been an "anode pressure" as suggested by Hamburger,¹²³ and by Skaupy,¹²⁴ it would have been noted.

4. *Electrical Operating Characteristics of the Mercury Arc.* The early knowledge of this field was summed up by Buttolph.¹²⁵ The following account is based largely upon his more recent accounts.¹²⁶

On starting the Uviarc lamp, the vapor pressure is low, as the lamp is cool, and the current is high and the voltage low. The lamp requires a short time to reach normal operating conditions, depending upon the heat capacity of the mercury cathode and arc tube, and upon the initial arc energy. As the temperature rises, the vapor pressure and the voltage follow, while the current drops. Normal opera-

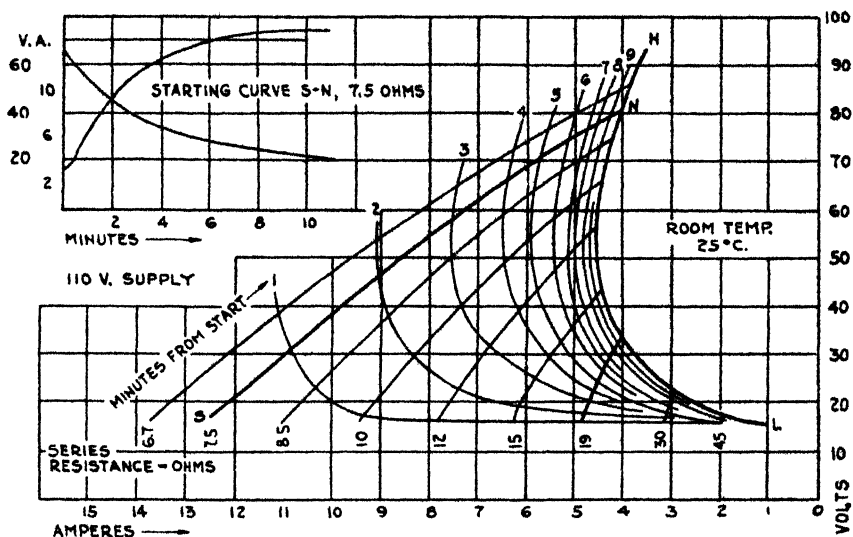


FIGURE 37. Starting and Operating Curves of Vertical Uviarc (Buttolph, *Review of Scientific Instruments*).

tion is reached when heat is radiated from the burner at such a rate that the vapor pressure no longer rises. In the upper left hand corner of Figure 37 the change in voltage and in current which occur during the first few minutes after starting are separately plotted and show clearly the way in which the arc comes to normal operation. As the starting current and the final arc voltage are each determined by the series resistance, a family of starting curves for different values of the series resistance is given in the main portion of the figure. The locus of the terminations of these curves at operating equilibrium at 25°C., H-L, is called the stationary or static characteristic curve for that arc at that temperature.

During the transition from the low pressure arc starting condition to the high pressure arc, there occurs a striking change in the appearance of the luminous arc column. As seen through a dark filter, the principal light source becomes concentrated in the center of the arc tube as a slender cord of great brilliancy. In this

¹²³ Hamburger, L., *Proc. Acad. Sci. Amsterdam*, **25**, 1045 (1917).

¹²⁴ Skaupy, F., *Verh. Dent. Phys. Ges.*, **19**, 264 (1917).

¹²⁵ Buttolph, L. J., *Gen. Electric Rev.*, **23**, 741, 858, 909 (1920).

¹²⁶ Buttolph, L. J., *Rev. Sci. Instruments*, **1**, 487 (1930); *Trans. Illum. Eng. Soc.*, **28**, 153 (1932).

condition there is about 25 volts drop per inch in the arc as compared with approximately $1\frac{1}{2}$ volts per inch in the low-pressure arc.

The Uviarc may be operated at various arc voltages from about 20 volts up to a maximum, characteristic of each size of lamp. The static characteristic curve H-L expresses the relationship between the arc voltages and the corresponding normal current. A significant feature is the steepness of the curve. The temperature at which there is normal operating equilibrium is determined largely by the temperature of the room and the ventilation of the burner. For example, with a given maximum burner voltage determined by the line voltage and the series resistance, the current normal for the design is increased by cooling the burner, as indicated by Figure 38. It is thus evident that the temperature of operation introduces

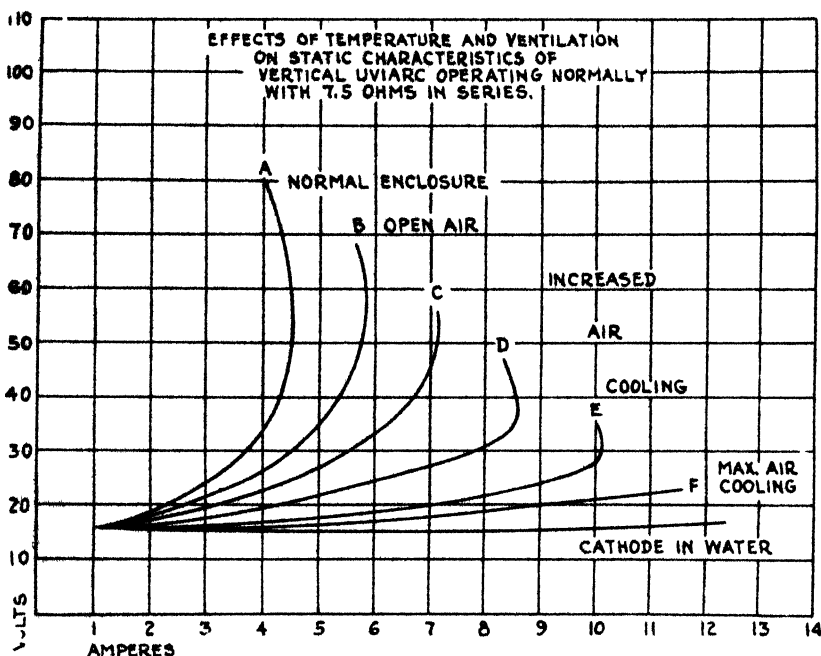


FIGURE 38. Effect of Temperature and Ventilation (Buttolph, *Review of Scientific Instruments*).

another variable. For this reason, the 220-volt horizontal Uviarc requires about 4.5 amperes at 165 volts between the electrodes when operated in open air, while its normal current when enclosed is only about 3.75 amperes at 174 volts on the arc. To secure a relatively increased intensity of radiation in the 2537A line, Uviarcs may be immersed in water to various depths depending upon the effects desired. Depending upon the temperature, the arc voltage then does not rise to more than 20 to 40 volts at 4 to 5 amperes. Wood¹²⁷ made use of this method

When so operated, the arc has the volt-ampere characteristic of a low-pressure arc, although the current density in the arc is greatly in excess of that obtainable

¹²⁷ Wood, R. W., *Phil. Mag.*, 50, 761 (1925); compare also Taylor, H. S., *J. Am. Chem. Soc.*, 48, 2489 (1926).

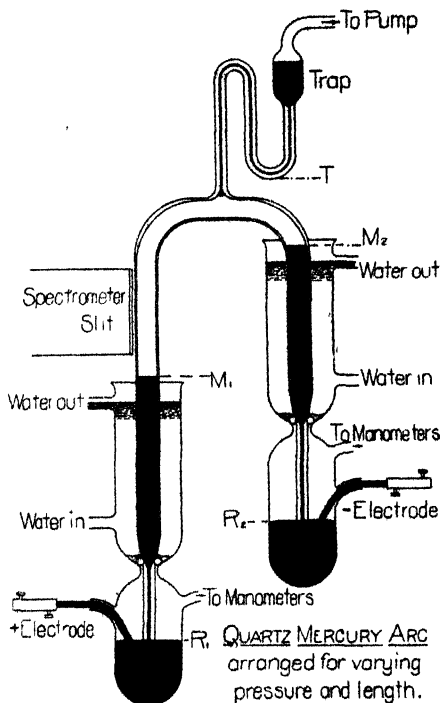
under conditions of temperature equilibrium in open air. This is an inefficient operating condition. The inlead wires are not intended to carry the excessive currents which may pass. Spattering from the tungsten anode is also greater than during operation at the same current and higher vapor pressures.

It is clear that the arc voltage drop depends upon the vapor pressure of the mercury, the mean vapor density of which increases with the temperature. The Uviarc dissipates about 50 watts per square inch of its silica tube, its mean temperature is about 360°C. , and the vapor pressure about 800 mm. These are maximum ratings based on an economic life of 6000 hours of continuous operation.

Among the first thorough studies of the static characteristic curves of the mercury arc were those of Harrison and Forbes,¹²⁸ who clearly appreciated the possibility of following changes in voltage with constant current by altering the ventilation of the arc. They also showed the negative characteristic in certain regions of the static curve; an increase in applied voltage produces a decrease in the current. When it gets too hot the lamp goes out.

FIGURE 39.

Special Design of the Harrison and Forbes Experimental Mercury Arc (*Journal of the Optical Society of America*).



For their work on the influence of current and voltage on the spectral distributions of the radiations, they designed a special lamp with variable length. (Figure 39.) The results were reduced to unit length after deducting the electrode drop in voltage, taken as 12 volts. Legs of an inverted copper U dipped into two Pyrex reservoirs, sealed to them by de Khotinsky cement, the upper part of each serving as water-cooler and the lower containing mercury for the arc. Iron wires sealed into the sides of the reservoirs dipped almost to the bottom of the mercury pools. A quartz trap was sealed to the top of the arc, so that the last traces of air in the tube could be exhausted by boiling the

¹²⁸ Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, 10, 1 (1925).

mercury up into the trap. When the lower legs and trap tube were of large bore, the arc had a great tendency to oscillate, the mercury levels moving up and down several centimeters and the arc-voltage varying by 20 per cent or more. To damp the oscillations down to a few hundredths of a millimeter and to keep the voltage constant, these legs were replaced below the water-coolers by quartz capillaries of 1 mm. internal diameter, the finest thread of mercury that would carry the maximum current of 5 amperes.

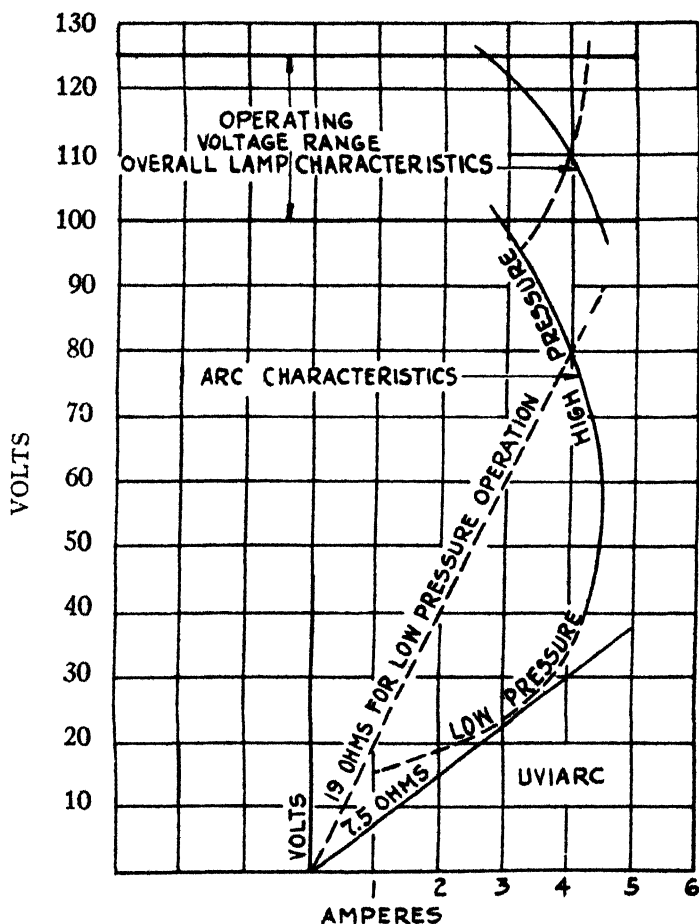


FIGURE 40. Regulation Characteristics for Slow Changes of Line Voltage (Buttolph, *Review of Scientific Instruments*).

The bands of the upper part of the tube were made with thickened walls to prevent fusion under the greater heat caused by deflected ions. The two reservoirs and trap were connected to vacuum through rubber pressure tubing by stopcocks, so that any one could be separately exhausted either through an inch of thermometer capillary or through a tube of large bore. Exact control of all mercury levels was possible. Air pressure up to two atmospheres could also be supplied to the reservoirs. Their pressures could be read from manometers.

In starting, both reservoirs and the body of the lamp were exhausted to a fraction of a millimeter and then mercury was allowed to rise slowly in the arms. The outside

of the lamp was heated by a Bunsen burner and the mercury boiled vigorously. When it had risen so as to fill partly the trap, the rubber tube connecting this to the pump was closed with a pinch-cock as near the trap as possible. The current was then turned on, the upper electrode being negative. The two reservoirs were then slowly exhausted until the mercury broke at the top of the U, and the arc length then increased as the pressure was built up in the tube. The height of the mercury columns was finally adjusted by varying the resistance in series with the lamp, the rate of cooling, and the pressure in the two reservoirs. Although the upper reservoir gradually filled at the expense of the lower, the excess could be returned without extinguishing the arc. A copper tube with small holes was bent to the shape of the quartz tube and air currents were directed on the whole luminous column when necessary. With this apparatus, a change could be made from one stationary state to another on a different characteristic curve much more rapidly than in the ordinary arc. The pressure could be built up rapidly in the arc when first struck by lengthening it to 25 cm., putting a large current through it, and then shortening the column, thus building up the voltage drop. The whole arc was enclosed in a large box with holes to provide variable degrees of ventilation. In series with the arc was a fairly high inductance to damp out oscillations and a variable maximum resistance of 200 ohms capable of carrying 5 amperes. The arc was fed by a 550-volt direct current generator, run on an induction motor. In no case was the voltage drop across the arc greater than 300 volts, or 17 volts per centimeter. Langmuir¹²⁰ also developed a cooled arc for the study of the characteristics of arcs at different vapor pressures.

By combining the "static" characteristic of the arc (H-I, Figure 37) with the volt-ampere characteristic of the fixed series resistance to be employed with it, there is obtained the volt-ampere curve of the actual working combination, shown in full lines in Figure 40. The use of greatly increased resistance to secure low pressure operation of the Uviarc is also shown in broken lines. The curved line marked "high pressure" is the supply voltage less the voltage drop in the series resistance and so represents the voltage available for operation of the arc at various stable arc currents. For the arc to be stable, the slope of this curve must be such that for various line voltages the voltage available for arc operation is never less than the arc drop. Buttolph emphasizes that the arc voltage is related to the current only indirectly through its ability to change the temperature and therefore the vapor pressure of the mercury. The positive volt-ampere characteristic of the Uviarc secures good "regulation" (change of voltage with current) only for very slow changes in the supply voltage which permit the attainment of temperature equilibrium.

The practical stability characteristic of the arc is better indicated by a family of "dynamic" regulation curves, such as are indicated by the series of arrow-marked lines of Figure 41. This shows the effect of sudden changes in supply voltage so rapid as to make the immediate effect of temperature changes negligible. The arrow-marked lines show approximately what happens as a result of sudden changes in supply voltage to new voltages maintained until temperature equilibrium has been attained. Since the apparent resistance can change only with the vapor pressure, the first effect of an increase in the supply voltage is only an increase in the arc current. With the resulting temperature increase, the arc voltage increases, the series resistance voltage decreases, the current decreases and normal operation is resumed at a higher arc voltage with practically the original current. A sudden change back to the normal and original voltage results in a completion of the cycle in a manner identical with that indicated for sudden decreases from normal. For transient voltage fluctuations, this cycle becomes greatly distorted and at high frequencies finally degenerates to changes only along the line LNH. The fact that the Uviarc current only affects the arc voltage rather slowly through the arc tempera-

¹²⁰ Langmuir, I., *Gen. Electric Review*, 27, 538 (1924).

ture, affects its apparent static instability, the cycle shown by the lines $L'N'H'$ requiring a relatively long time for completion. The curve marked "arc watts" shows that a condition of energy and temperature maximum exists at approximately the normal operating voltage. The "regulation" of the lamp depends upon the amount of series resistance used; this is determined by the permissible arc current fluctuation and the local variation in power supply voltage.

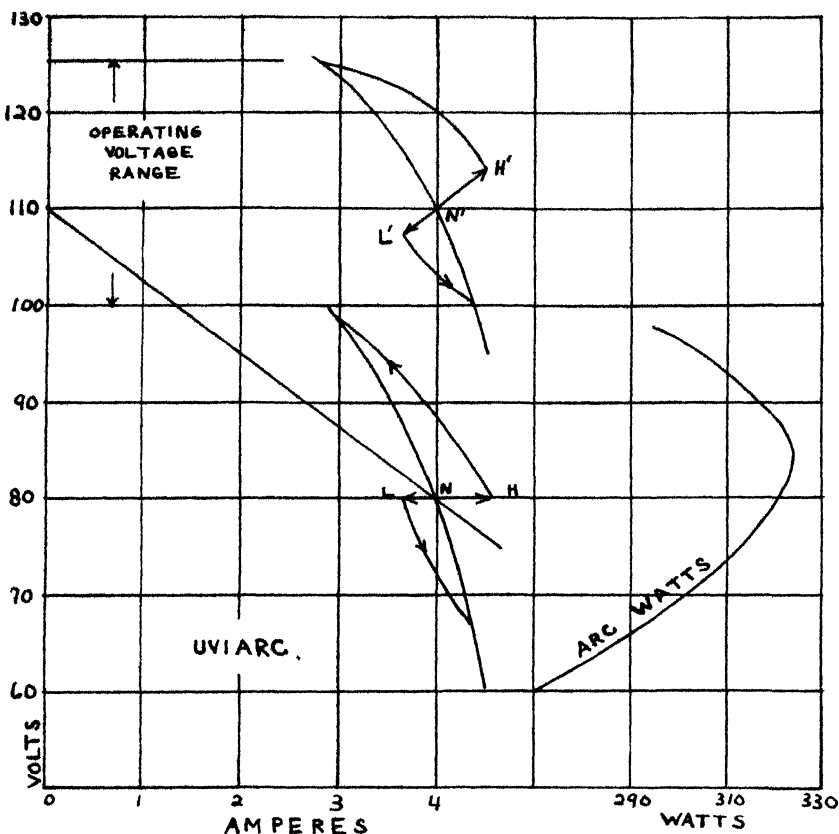


FIGURE 41. Regulation Characteristics for Sudden Changes of Line Voltage (Modified from Buttolph, *Review of Scientific Instruments*).

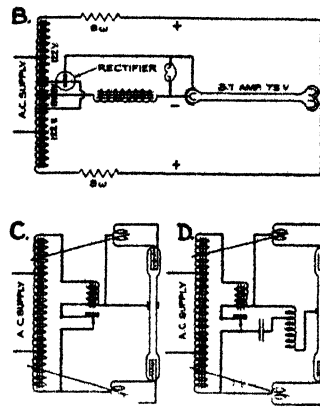
There is also an inherent instability of the arc, related to changes in its apparent resistance, and ascribed to transient high-frequency variations of the current. This appears to be a cathode phenomenon, the cause of which is not definitely known. These current variations are most pronounced during low-pressure operation at starting and result in an arc-extinguishing effect opposed only by the impedance of the circuit. The arc and its supply line act much like a series resonant circuit. The frequency of the oscillations may be several thousand per second; several thousand volts may be induced on the arc terminals, resulting in transient reductions of the current to amounts insufficient to maintain the arc. This form of instability may be largely eliminated by inserting sufficient resistance to absorb one-third of the

supply voltage. In practice, one-quarter henry (or for a very unstable direct-current supply line or for rectifiers with pulsating output, one-half henry) in an open-core inductance connected in series with the arc and as directly as possible to the cathode, permits stable operation with about 10 per cent greater voltage on the arc than would otherwise be possible.

The arc is essentially a direct current device because the cathode cannot be maintained active on alternating current half-time operation. It may, however, be operated upon alternating current by using a rectifier circuit and an arc with two anodes. (See Figure 42.) The cathode is connected to the secondary midpoint of a transformer, and the anodes are connected to its terminals. The series resistance may be in two sections placed adjacent to the anodes, or in a single unit placed either between the arc cathode and the transformer or in series with the primary. Either the anodic or the primary positions are preferable. The mercury cathode remains continually negative relative to either one anode or the other at all times,

FIGURE 42.

Circuits for Alternating Current
Mercury Arc (Buttolph, *Transactions*
Illuminating Engineering Society).



being maintained through zero supply voltage by the cathode inductance. The electron stream passes from the cathode to one anode during the active half-cycle, to the other anode during the following half-cycle, and to both anodes during the transition. The inductance has the new function of maintaining the arc current at a level sufficient to keep the hot spot alive during zero voltage. This effect can be secured by using a transformer of sufficient magnetic leakage and even the regulating resistance can be replaced by reactance, but either of these changes causes so great a lowering of the power factor as to be impracticable. Buttolph¹³⁰ gives a detailed analysis of typical oscillograms, which lies beyond the scope of this book.

The starting of the alternating-current arc is complicated by the fact that the starting circuit is, in effect, connected to but one of the two anodes, and that the current flowing in the shifter circuit is alternating and hence is of the correct polarity for arc starting but one half of the time. A further limitation to the use of this method in the starting of the alternating-current type of arc lies in the fact that to secure a satisfactorily high induced potential, the negative inductance or choke must be of so high a value that a potential of about 120 volts must be applied to the starting circuit in order to secure a satisfactory shifter current. This causes great stability in the shifter arc, resulting in a trailing of the shifter arc through to the extreme end of the half cycle in which the mechanical break occurs. Figure 42B shows a solution of several of these problems¹³¹ through the use of a small dry rectifier supplying about one ampere of

¹³⁰ Buttolph, L. J., *Rev. Sci. Instruments*, 1, 500 (1930).

¹³¹ Buttolph, L. J., *Trans. Illum. Eng. Soc.*, 28, 153 (1932).

rectified direct current of just sufficient voltage to cause a flow of about one ampere through the inductance. The impedance of even one-third henry choke to this pulsating direct current is so low that the equivalent of only about a three- or four-volt direct current supply is required to secure a shifter current of over one ampere.

Other starting methods as a choke and either a mercury switch or a mechanically operated circuit-breaker may be used to secure high voltage transients sufficient to ionize the gas and start the discharge in the ordinary type of alternating current arc. (Figure 42C.) An alternative to the relatively slow action of a mercury interrupter or of a mechanically vibrating interrupter is the use of a simple oscillatory circuit (Figure 42D) in which there is imposed on the arc tube a high-voltage, high-frequency impulse, the high-frequency nature of the discharge being effective through the use of an external electrode placed preferably somewhere near the center of the arc tube.

A detailed treatment, based upon studies with the oscillograph, has been given by Buttolph and Dana.¹²³

THE MECHANISM OF THE EMISSION OF RADIATION

The radiation emitted by the Uviarc extends from the 10,140Å¹²³ line in the infrared to the region of 1850Å in the ultraviolet. The energy-level diagram of mercury given in Figure 4 (Chapter 2) forms the basis for an interpretation of the lines emitted in terms of the impacts of electrons possessing the necessary kinetic energies. The connecting lines between the various energy states represent most of the lines of the arc spectrum of mercury. It has been stated in the preceding section that very small fractions of the current are carried by ions of valence higher than one. The presence of such ions makes it possible that some of the lines of the emission spectrum of the mercury lamp may be ascribed to transitions which would find their representations on other energy level diagrams for the corresponding ions; these are, however, of little significance.

The diagram indicates that the two resonance states produced by impacts of 4.87 and 6.67 electron-volts produce lines in the ultraviolet at 2537 and 1849Å, respectively. The various visible lines are produced by transitions from higher energy levels to the lowest excited levels corresponding to the resonance potentials or to a metastable state.

The metastable states of the mercury atom are energy levels from which there occur no transitions with emission. The diagram indicates that 7.7 volts (applied in two stages) produces an energy level 2^8S_1 , from which the green line 5461Å is emitted, the atom falling into a metastable state, 2^3P_2 . A second metastable state, 2^3P_0 , is produced similarly by a transition from the 2^8S_1 state with emission of the 4047Å line. While the usual higher energy level states have a duration of about 10^{-8} second, the metastable states persist for times of the order of 10^{-8} to 10^{-4} second.¹²⁴ The metastable states can also be reached from the normal states by direct electron impacts, but the direct transition from a metastable to a normal state is very improbable, so much so that the lines corresponding to such transitions are "forbidden" lines. Various processes limit the existence of an atom in a metastable state. Another electron can hit it and raise it to a higher energy level or even ionize it. It may suffer impact with another atom and gain or lose energy thereby. In the presence of a gas with a lower resonance or ionization potential, the metastable atom may yield some of its energy to one of the foreign atoms, raising it to a higher energy level or ionizing it.

¹²³ Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, 4, 209 (1933). Note also Kelting, R. C., U. S. P. 2,152,998, Apr. 4, 1939.

¹²⁴ For the infrared arc spectrum of mercury, see Wiedermann, G., and Schmidt, W., *Z. Physik*, 106, 273 (1937); Murakawa, K., *Z. Physik*, 108, 168 (1938).

¹²⁵ Methods for the determination of these life periods for various energy level states lie beyond the scope of this book. See Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge, 1934.

Since in the operation of the usual forms of the mercury arc all the arc lines are emitted in addition to the resonance lines, the conditions must be such as to enable the bombarding electrons to raise the mercury atoms to the energy level corresponding to the ionization potential of 10.4 volts, although the voltage drop at the cathode by which the electrons are accelerated is only about 10 volts. Compton¹³⁵ suggested that the ionization must be produced as a result of two impacts. The electron energy is close to that required for the production of meta-stable atoms (see Figure 4) or to ionize these when formed.

The intensity of a line depends upon the fraction of the atoms in process of transition from a higher to a lower state; this depends upon the concentration of higher state atoms. This in turn varies directly with the electron current and the concentration of the atoms in the lower state, that is, with the current and pressure. Furthermore, the velocity of the electron must be sufficient to effect the transition in question; this depends on the voltage gradient in the region in which the electron acquires its velocity. For forming the 2^1P_1 state of mercury (6.67 volts), the probability of excitation increases from zero at 6.67 volts to a maximum at 6.8 volts, after which it decreases.¹³⁶ Similar considerations apply to each of the other states; the varying probabilities of excitation to each of these states under operating conditions accounts for the varying intensities of the lines which correspond to transitions from these states.

The theory is, however, much more complex, since the intensity of a line depends not only on the probability of formation of the necessary energy state, but also upon the probability of the transition from that state. This is true since other transitions from that state producing other lines may also occur. In place of dropping to one of several lower excitation states with emission of the corresponding lines, it may also be raised to a still higher state of excitation by suffering impact with an electron. The further analysis of these probabilities of emission, collision or ionization depends upon the determination of the mean free paths of the atoms and of their effective radii for collisions.

The uniformity of the light emitted along the lengths of the positive column shows that the electrons must acquire energy from some source other than the cathode fall. It comes from the energy input into the column, the product of the arc current into the voltage gradient. The latter factor depends upon the current density and the pressure. Schottky¹³⁷ believed the voltage gradient to vary inversely with the tube diameter. For mercury vapor, Güntherschulze¹³⁸ found at different pressures that the gradient is a function of the tube diameter, d , and the

current I , $X = \frac{c}{d^a I^b}$, a , b , and c being constants. The values of a and b vary with the pressure of the mercury vapor. At 100°C., a is 0.69 and b is 0.12.

Within the positive column, the average kinetic energy of the electrons is too low to excite or ionize the mercury atoms. There is, however, a Maxwellian distribution of the kinetic energy among the electrons, so that a small fraction of them do have a sufficient amount of energy to produce these effects. The average kinetic

¹³⁵ Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); see also Mason, R. C., *Phys. Rev.*, **38**, 427 (1931); Gehrtz, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932); Barnes, B. T., and Adams, E. Q., *Phys. Rev.*, **53**, 545, 556 (1938); Fabrikant, V. A., Butaeva, F., and Tsirg, *Fizik. Z., Sowjetunion*, **13**, 23 (1938); *Chem. Abs.*, **31**, 8352 (1937); **32**, 4871 (1938).

¹³⁶ Brattain, W. H., *Phys. Rev.*, **34**, 474 (1929).

¹³⁷ Schottky, W., *Fizik. Z.*, **25**, 342, 635 (1924).

¹³⁸ Güntherschulze, A., *Z. Physik*, **41**, 718 (1927); **42**, 763 (1927) (glow discharge). See also Elenbaas, W., *Physica*, **5**, 568 (1938); *Chem. Abs.*, **32**, 7340 (1938).

energy ($3/2 kT_e$) depends upon the electron temperature T_e . Killian¹³⁹ studied the effects of pressure upon the electron temperature and total electron concentration over a low pressure range in a mercury arc in a tube of 6.2 cm. diameter, carrying a current of 5 amperes. The electron temperature decreased from 38,000°K. at 0.00020 mm. to 19,900°K. at 0.00533 mm. An electron temperature of 19,900° means that the average kinetic energy of the electrons is 2.56 volts. The fraction of the electrons having kinetic energies greater than the ionization potential of mercury is in this case, from the Maxwell-Boltzmann distribution law, about 0.003.¹⁴⁰ The energy lost by this small fraction of the electrons in ionizing collisions is supplied by the energy input into the positive column. Killian found also that an increase in pressure increased the probability of collisions, although it reduced the electron temperature. These opposing effects cause the emission at constant current density to pass through a maximum as the pressure is increased. Other observations showed that the electron temperature tends to decrease somewhat with an increase in the arc current. In Killian's experiments, the average electron concentrations varied between 3.7×10^{10} and 15.2×10^{10} per cubic centimeter as the pressure was increased from 0.00020 mm. to 0.00533 mm. The theory of Tonks and Langmuir¹⁴¹ indicates that there is also a concentration gradient for electrons from a maximum along the axis of the tube toward the walls. Not all of the energy input into the positive column is utilized in excitation or ionization. Some of the energy is delivered to the walls, being liberated there by the recombination of electrons and ions. As the electron temperature was decreased from 38000°K. to 19,900°K. in the experiments of Killian the energy delivered to the walls by recombination processes could be calculated to decrease from 48 to 14 per cent of the total input. The remainder was available for excitation processes.

These experiments do not apply directly to the usual types of mercury arc, since the pressure range is quite different. Lübecke¹⁴² finds that the electron temperatures are 7000 to 40,000°K. in the more usual forms.¹⁴³

CONTINUOUS AND BAND SPECTRA IN THE MERCURY ARC

The line spectrum of mercury is superposed upon a fainter continuous spectrum, emitted by glowing vapor distilling from the arc. It has been in part attributed to incandescence. The continuous spectrum, together with the selective absorption of the luminous mercury vapor for its own radiation, in part accounts for a shift in the relative radiation intensity toward the longer wave-lengths with increased energy input, in contrast with Wien's displacement law. A review of continuous emission spectra in general has been given by Finkelburg.¹⁴⁴

Volkringer¹⁴⁵ observed a large band at 3360Å and a smaller one with a maximum at 2650Å. Dawson and Crew¹⁴⁶ found band maxima in the arc at atmospheric pressure, excited by high voltage and low current density, at 4500, 3300 and 2550Å. No continuous radiation was emitted in the region 2535 to 2350Å. On increasing

¹³⁹ Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).

¹⁴⁰ For further details of such calculations, see Dushman, S., *Elec. Eng.*, **53**, 1204, 1283 (1934).

¹⁴¹ Tonks, L., and Langmuir, I., *Phys. Rev.*, **34**, 876 (1929).

¹⁴² Lübecke, C., *Z. tech. Physik*, **14**, 298 (1933).

¹⁴³ For further details of probe tests in various mercury arcs, see Lübecke, C., *Z. tech. Physik*, **8**, 445 (1927); Gvozdozer, S. D., and Konovalov, F., *Compt. rend. acad. Sci. U.R.S.S.*, **1**, 553 (1934); *Chem. Abs.*, **28**, 4975 (1934); Togo, S., *J. Inst. Elec. Eng. Japan*, **53**, 109 (1933); Klyarfel'd, B., and Flokhotzki, E., *Z. tech. Physik (U.S.S.R.)*, **5**, 796 (1934); *Chem. Abs.*, **29**, 673 (1935).

¹⁴⁴ Finkelburg, W., *Physik. Z.*, **31**, 1 (1930). See also Rompe, R., Schulz, P., and Thouret, W., *Z. Physik*, **112**, 369 (1939); Unsöld, A., *Ann. Physik*, **33**, 607 (1938).

¹⁴⁵ Volkringer, H., *Compt. rend.*, **185**, 60 (1927).

¹⁴⁶ Dawson, L. H., and Crew, W. H., *J. Opt. Soc. Am.*, **17**, 261 (1928).

the current, the bands broadened in both directions and filled this gap. Crew and Thornton¹⁴⁷ attribute the bands to the Hg_2 molecule produced at the distilling surface of the mercury and readily dissociated even by slowly moving electrons or ions. From the intensity of the band at 2540Å at various temperatures and pressures, Koernicke¹⁴⁸ calculated the heat of dissociation of the molecule to be 1.4 kcal. Nakamura¹⁴⁹ regarded the 2536Å band as due to the arc type of excitation of the neutral molecule and the band at 2540Å as due to the ionized molecule Hg_2^+ .¹⁵⁰

¹⁴⁷ Crew, W. H., and Thornton, W. N., *J. Opt. Soc. Am.*, **19**, 358 (1929).

¹⁴⁸ Koernicke, E., *Z. Physik*, **33**, 219 (1925).

¹⁴⁹ Nakamura, G., *Mem. Coll. Sci. Kyoto*, **10**, 1 (1926); *Chem. Abs.*, **21**, 1755 (1927).

¹⁵⁰ For recent studies of the origin of the mercury bands, see Lord Rayleigh, *Nature*, **119**, 423, 778 (1927); **127**, 125, 854 (1931); *Proc. Roy. Soc.* **116A**, 702 (1927); **119A**, 349 (1928); Kuhn, H., *Naturwiss.*, **16**, 352 (1928); *Z. Physik*, **72**, 462 (1931); Ponte, M., *Compt. rend.* **186**, 633 (1928); Winans, J., *Nature*, **121**, 863 (1928); Pienkowski, S., *Bull. intern. Acad. Polonaise*, Nos. 4-5A, 171 (1928); *Chem. Abs.*, **23**, 2103 (1929); Dziedzicki, N., *Compt. rend. soc. polonaise Phys.*, **3**, 207 (1928); *Chem. Abs.*, **23**, 5095 (1929); Hulubei, H., *Compt. rend.*, **193**, 154 (1931); Hamada, H., *Phil. Mag.*, **12**, 50 (1931); Winans, J., *Phys. Rev.*, **37**, 897, 902 (1931); **39**, 745 (1932); **42**, 800 (1932); Okubo, J., and Matsuyama, E., *Nature*, **129**, 653 (1932); *Science Repts. Tohoku Imp. Univ.*, 1st series, **22**, 383 (1933); *Chem. Abs.*, **27**, 5642 (1933).

Chapter 7

Output of the Mercury-vapor Lamp Under Various Operating Conditions

METHODS OF MEASURING THE INTENSITY OF THE RADIATIONS

The evaluation in absolute energy units of the radiations in various lines or wave-length regions emitted by a radiation source is difficult and requires means for the isolation of various wave-length bands by filters or monochromators as well as means for measuring the energies radiated within these bands. To avoid the difficulties involved and the apparatus required for such measurements a number of workers have described photochemical reactions which indicate the effectiveness of a radiation source for conducting photochemical changes. Many of these reactions are of little value, and even the better ones require a critical understanding of all the physical factors involved if they are to be employed effectively.

Among the apparatus used for measuring the quantity of radiant energy are thermopiles. When it is desired to express the results in absolute units of energy, the thermopiles must be calibrated against some standard source of energy. Thermopiles are non-selective and measure radiant energy of any wave-length. Their use is described in the following references, those by Coblenz giving detailed directions¹ for the construction, installation and use of these instruments. More recent descriptions have been given by Strong² and Cartwright³; precautions in the use of these instruments have been given by Leighton and Leighton.⁴

Mere exposure of a thermopile to a source gives information only as to the total energy emitted, but tells nothing of the distribution of radiations among the various spectral regions. To measure distribution in the ultraviolet region a quartz monochromator, by means of which the wave-lengths can be separated into very narrow bands, is frequently employed with the thermopile.⁵ When using thermopiles with quartz monochromators, correction should be made for slit width,⁶ aberrations, reflection, absorption, and scattering in the optical train. McAlister⁷ has described in detail the use of two quartz monochromators for determining absolute ultraviolet intensities by the aid of vacuum thermopiles and Photronic cells.

It is possible, however, to obtain information regarding the spectral distribution

¹ Coblenz, W. W., *Bur. Standards Bull.* 4, 391 (1908); 9, 7 (1913); Moll, W. J., and Burger, H. C., *Z. Physik*, 32, 575 (1925); Coblenz, W. W., *J. Opt. Soc. Am.*, 5, 259 (1921); Voegelé, W., *Physik. Z.*, 22, 119 (1921).

² Strong, J., *Rev. Sci. Instruments*, 3, 65 (1932).

³ Cartwright, C. H., *Rev. Sci. Instruments*, 3, 73 (1932).

⁴ Leighton, P. A., and Leighton, W. G., *J. Phys. Chem.*, 36, 1882 (1932).

⁵ For a critical discussion, see Forbes, G. S., Report of the Committee on Photochemistry of the Division of Chemistry and Chemical Technology of the National Research Council, *J. Phys. Chem.*, 32, 491 (1928).

⁶ Coblenz, W. W., Dorcas, M. J., and Hughes, C. W., *Bur. Standards Sci. Paper*, 21, 535 (1927); Coblenz, W. W., *Bur. Standards Bull.* 10, 41 (1914); 17, 1 (1920); Franklin, R. G., Maddison, R., and Reeve, L., *J. Phys. Chem.*, 29, 713 (1925).

⁷ McAlister, E. D., *Smithsonian Miscellaneous Collections*, 87, No. 17 (1933).

of the energy emitted by a source, by employing filters for delimiting various ultraviolet regions.⁸ Such methods are illustrated in the work of Gillam and Morton discussed below in connection with chemical actinometers. Stockbarger and Burns⁹ have reported methods for standardization of the conditions to be met in the use of filters, which methods are discussed in more detail in Chapter 10. In general, the infrared energy, the energy in successively shorter-wave regions of the visible and the energy in the ultraviolet range are measured in successive experiments with the corresponding filters. The energy introduced in each of the increments is calculated by differences. The equivalent wave-length range of the increments is approximated from the filter transmission curves.¹⁰ Fabry and Buisson¹¹ measured the total energy L transmitted by n different filters, of thickness d (or n different thicknesses of the same filter). They solved n equations of the form $L = A_1 e^{-m_1 d}, \dots, A_n e^{-m_n d}$ for $A_1 \dots A_n$, the n monochromatic intensities of the original source; $m_1 \dots m_n$ were determined separately for each filter.¹²

Also, photoelectric cells have been used for energy measurements. Such cells have almost linear intensity-current curves, and are free from time-lag, fatigue and deterioration. Their use, however, requires a knowledge of the sensitivity regions of the various cells, since these cells are selective in their response to particular wave-length regions. When the measurement is intended to serve as an indication of the suitability of a source for effecting a given photochemical change, the wave-length region necessary to bring about the reaction must be known in order that the appropriate photo-cell may be selected.

Elster and Geitel¹³ used a zinc sphere for measuring ultraviolet radiation through photoelectric effect. Szillard used cadmium in the cathode of a photoelectric cell sensitive to the region 2950 to 3900A. Griffith,¹⁴ by employing a quartz window to the above cell, made it sensitive to 2000A and with Taylor¹⁵ adapted it to the photometry of therapeutic lamps. Harris¹⁶ replaced the electrometer or gold-leaf electroscope used in conjunction with such cells by more robust measuring apparatus. He adapted a thermionic valve and microammeter to a circuit employed for the measurement of the output of a quartz mercury arc. Miethe and Stenger¹⁷ used a silver film, and Anderson¹⁸ has described a method of measuring and controlling the total ultraviolet output from a quartz mercury arc by using the Weston "Photronic" light-sensitive cell.

An ultraviolet light meter described by Rentschler¹⁹ comprises special uranium, thorium, cerium, titanium and tantalum photoelectric cells connected to a glow relay tube. The latter consists of an iron cathode, a thorium starting anode and a main anode contained in an inert gas atmosphere. The intensity of incident radiations is proportional to the rate at which an electromechanical counter actuated by the glow tube registers. The total energy is measured by a recording

⁸ See Krefft, H., and Rössler, F., *Z. tech. Physik*, **17**, 479 (1936).

⁹ Stockbarger, D. C., and Burns, L., *Phys. Rev.*, **34**, 1263 (1929).

¹⁰ Coblenz, W. W., Long, M. B., and Kahler, H., *Bureau of Standards Bull.* **15**, No. S 330 (1918).

¹¹ Fabry, C., and Buisson, H., *Compt. rend.*, **152**, 1839 (1911).

¹² Coblenz, W. W., and Kahler, H., *Bur. Standards Bull.* No. 378 (1920). Ornstein, L. S., *J. phys. radium* (7), **4**, 613 (1933). Kawa, J., *Towarzystwa Fiz.* **4**, 27; *Chem. Abs.*, **25**, 2361 (1931).

¹³ Elster, J., and Geitel, H., *Physik. Z.*, **12**, 609 (1911); **13**, 739, 852 (1912).

¹⁴ Griffith, H. D., *Lancet*, 5th December, 1205, 1925.

¹⁵ Griffith, H. D., and Taylor, J. S., *J. Hyg.*, **25**, 218 (1926).

¹⁶ Harris, D. T., *J. Sci. Instruments*, **6**, 2 (1929).

¹⁷ Miethe, A., and Stenger, E., *Z. wiss. Phot.*, **19**, 57 (1919).

¹⁸ Anderson, W. T., Jr., *Rev. Sci. Instruments*, **5**, 127 (1934).

¹⁹ Rentschler, H. C., *J. Am. Inst. Elec. Eng.*, **49**, 113 (1930); see also U. S. P. 1,923,844, August 22, 1933.

meter. Cerium is photo active below 4500Å, thorium below 3700Å, uranium below 3200Å, titanium between 2700-3200Å, and tantalum between 2000-3000Å. A proper choice of metal and quartz or glass container allows radiations of definite wave-length bands to be measured. It has been employed, with some modifications, in the investigations on air pollution conducted at the Mellon Institute.²⁰ Figure 43 shows the wiring diagram of the Rentschler Ultraviolet Meter.²¹ The photoelectric cell shown on the central panel is mounted in a special glass bulb which admits all the ultraviolet reaching the surface of the earth. It has two electrodes, a central rod and a cathode of uranium, sputtered (in argon) over a small area of approximately 12 square centimeters on the inside wall of the bulb.

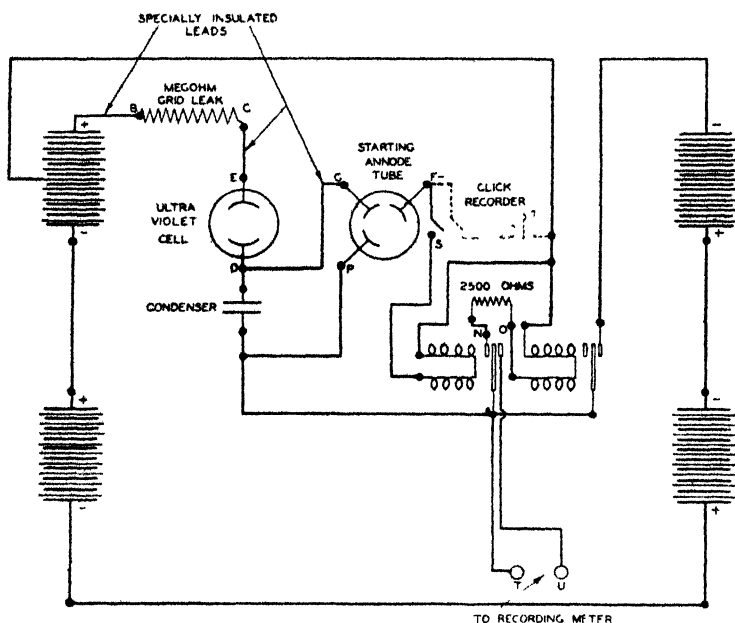


FIGURE 43. Wiring Diagram for Ultraviolet Meter (Meller, Hibben and Warga, *Transactions Illuminating Engineering Society*).

The uranium cathode, by emitting electrons, allows current to flow through the cell only when radiations between 2700 and 3350Å fall upon it. The current is proportional to the intensity of the radiation, but is very small (0.1 microampere) and requires amplification by a glow relay or starting anode tube. The current trickling through the cell slowly charges a condenser. When this reaches a fixed value, the condenser spills over and an impulse of current flows between its plates. The frequency with which this occurs is proportional to the intensity of the radiation. The current flow in the tube at this point operates either a click recorder or a graphic recording meter in which a moving pen integrates the impulses over

²⁰ Meller, H. B., Hibben, S. G., and Warga, M. E., *Trans. Ill. Eng. Soc.*, 27, 64 (1932).

²¹ Rentschler, H. C., and Henry, D. E., U. S. P. 1,815,073, July 21, 1931; British P. 353,981, June 12, 1929; Rentschler, H. C., U. S. P. 1,871,280, Aug. 9, 1932; 1,917,854, July 11, 1933; British P. 353,554 and 353,555. Special fluorescent filters for use in conjunction with such photo-cells have been described by E. D. Wilson, U. S. P. 2,128,110, Aug. 23, 1938; *Chem. Abs.*, 32, 7824 (1938).

a short time interval. The record discloses variations that may occur rapidly. The sensitivity of the uranium photo-cell, shown in Figure 44, is at a maximum between 2950 and 3000Å. Different cells have different sensitivities and each cell must be calibrated. According to Meller, Hibben and Wurga, the chief source of error is leakage to the ground or around the condenser. They calibrated their meter against a standard tungsten-ribbon lamp which, operated at 27.5 amperes, had a true temperature of 2800°K. The results are given in arbitrary units, the number of impulses per unit of time.

Dorno²² also finds the cadmium cell to be sensitive between 2800 and 3500Å. Coblentz and Stair²³ described a portable ultraviolet intensity meter comprising a photoelectric cell, balanced amplifier, and microammeter.²⁴ Coblentz²⁵ devel-

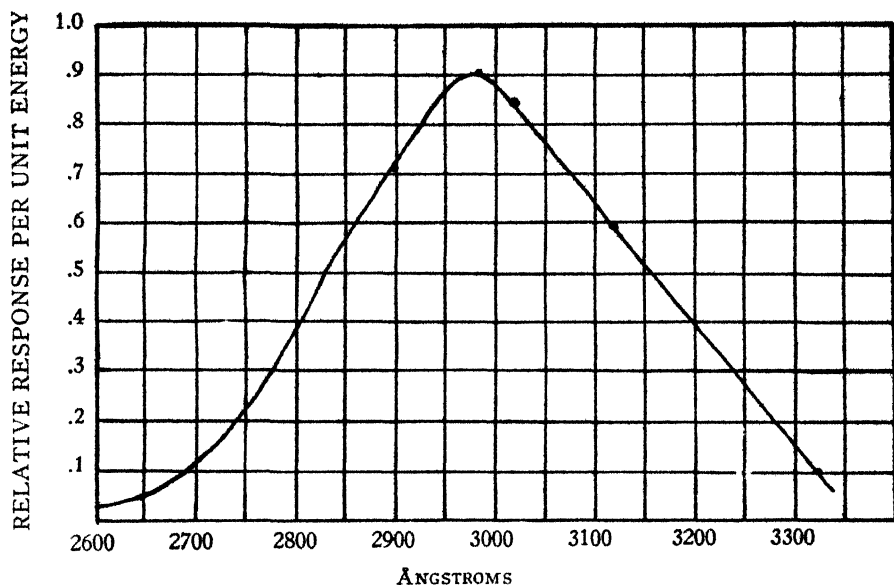


FIGURE 44. The Response or Sensitivity Curve of the Ultraviolet Photocell (From Meller, Hibben, and Wurga, *Transactions of Illuminating Engineering Society*).

oped a practical field method for determining the energy distribution of the sun in absolute units. Two methods were devised, one employing filters and a balanced thermopile calibrated in absolute value against a standard of thermal radiation. The other employed a titanium photoelectric cell calibrated in absolute value against a standard of ultraviolet radiation. For the latter, Coblentz and Stair²⁶ use a commercial vertical mercury-in-quartz arc.²⁷ It proved of especial value

²² Dorno, C., *Strahlentherapie*, 25, 361 (1928); *Chem. Abs.*, 22, 1540 (1928).

²³ Coblentz, W. W., and Stair, R., *Bureau Standards J. Research*, 12, 231 (1934).

²⁴ For further discussion of the calibration of photoelectric cells, or for the use of thermopiles and filters in measuring the energy distribution of sources, see Coblentz, W. W., *Science*, 76, 412 (1932); *Strahlentherapie*, 50, 179, 487 (1934); *Am. J. Roentgenol. Radium Therapy*, 33, 793 (1935); Coblentz, W. W., Stair, R., and Hogue, J., *Bur. Stand. J. Res.*, 7, 723 (1931); 8, 759 (1932); Coblentz, W. W., *Bull. Bureau Stand.*, 9, 51 (1912); 11, 87; *Bur. Stand. J. Res.*, 11, 79 (1933).

²⁵ Coblentz, W. W., *Puerto Rico J. Public Health Trop. Med.*, 11, 1 (1935); *Chem. Abs.*, 30, 118 (1936).

²⁶ Coblentz, W. W., and Stair, R., *J. Res. Bur. Standards*, 16, 83 (1936).

²⁷ Report of the Illuminating Engineering Society Subcommittee on the Measurement of Ultraviolet Radiation, *Trans. Illum. Eng. Soc.*, 28, 864 (1933).

as a standard for meters used to evaluate sources for germicidal and erythema-producing effects by the aid of the photo-cell. Since the cell is insensitive to wavelengths longer than about 3300Å, and since the short-wave response may be limited to about 2800Å by enclosing the cell in Corex D glass, practically only the strong emission lines at 2967, 3024 and 3132Å are effective. A gas-filled tungsten lamp has been employed occasionally as a standard, but a source emitting a continuous spectrum has several disadvantages over the discontinuous spectrum of the mercury arc.

One method of calibrating a photoelectric intensity meter in absolute values comprises observing the microammeter reading on exposure of the cell to a strong emission line of the mercury arc, *e.g.*, 2967Å, the energy value of which had been determined in absolute units. By dividing the scale reading by the efficiency of the photoelectric response for that wave-length, the true scale reading would be relatively the same as that of a spectrally nonselective radiometer. For reasons concerned with the construction of the photoelectric cell first employed by Coblenz, difficulties were encountered in attempting to operate it at the exit slit of the spectroradiometer used in isolating the 2967Å line. Therefore, it proved simpler to use the arc with a Corex D filter, so that the radiations effective on the photo-cell were limited (as before mentioned) to a few lines. The sum of these emissions could be accurately evaluated in absolute units with a balanced thermocouple and filters at the time the photoelectric measurements were made. Comparative reading would be taken at the same distance from the lamp in both instances. This obviates the effect of room temperature upon the output of the standard source. Alternatively, the lamp could be operated at a constant energy input in an inclosure maintained closely at the same air temperature, so that a single standardization of the lamp against the thermopile suffices until the lamp shows signs of ageing. This ageing (a blackening of the tube surrounding the tungsten anode) is eliminated, together with flickering at the cathode, by placing an aluminum diaphragm in front of the lamp to limit the emission to 30 millimeters at the central portion of the lamp. The lamp employed was the Cooper-Hewitt, 110-volt, vertical Uviarc mounted in a support which permits tilting the burner to a horizontal position for starting. A laboratory rheostat of about 18 ohms was connected in series. The potential was kept at about 5 volts below normal (70 volts) to decrease depreciation. The lamp and mounting may be kept in a ventilated, galvanized housing. When used with the diaphragm, the apparent depreciation is slow. Operated on a storage battery, the lamp remains constant at 65 ± 0.3 volts. This slow fluctuation of ± 0.3 volt is probably the result of changes in ventilation and is easily controlled with a rheostat, so that the ultraviolet output in a particular region is regulated within two or three parts in 1500.

Gyemant²⁸ described a fluorescent intensimeter for ultraviolet rays. A simple "UVscope" described by Alexander and referred to by Moss and Knapp was a filter of Chance's glass which absorbed all rays shorter than 3650Å, the longer transmitted rays being recorded by their effects on photographic paper. The Hanovia Co.²⁹ described an apparatus with a fluorescent screen and ammeter indicator from which the intensity of the light could be directly read.

The Geiger-Müller electron counter, widely used in cosmic ray measurements, has been employed for the measurement of an ultraviolet beam, by counting the electrons produced by the photoelectric effect of the beam. The counter is used

²⁸ Gyemant, A., *J. Opt. Soc. Am.*, **12**, 65 (1926).

²⁹ Croad, A. K., British P. 320,794, Nov. 8, 1928, to The Hanovia Co.; *Brit. Chem. Abs.*, **B**, 1021 (1929).

chiefly in the study of ultraviolet of very low intensities, such as the assumed mitogenetic rays.⁸⁰

Chemical Actinometers. Comparison of some chemical actinometers was given by Eidinow.⁸¹ Since the reactions depend upon the intensity of restricted wave-length regions, the results of such measurements may show apparent disagreement. In using chemical methods as a rough guide to the times of exposure required for a given reaction to be effected by a lamp, it is essential to select a test reaction which is effected in approximately the same wave-length region as that required for the reaction to be conducted. This is true since every photochemical reaction has its own characteristic curve of spectral sensitivity, while every light source has its own spectral energy distribution. Thus for controlling the bactericidal action of a lamp, it is necessary to choose as a test reaction one which is not effected by visible radiations or by those longer than about 2950Å. (See Chapter 35.) Dorcas and Forbes⁸² pointed out the necessity of using in conjunction with a chemical actinometer, a filter which transmits for each wave-length a fraction of incident radiation proportional to the efficiency of the radiation in promoting the reaction for which the light is intended to be employed. This method of measurement furnishes a comparison of the abilities of sources of different spectral distribution to effect a given reaction. In the case of skin erythema tests, taken as an index of biological stimulation, a filter comprising a one-centimeter thickness of 0.00025 molar picric acid between a sheet of red-purple Corex glass 2.5 mm. thick and one of clear Corex was utilized. This filter had an absorption curve bearing a resemblance to the Hausser and Vahle erythema curve⁸³ replotted on the basis of quanta rather than ergs. The replotting was done by multiplying the ordinates of the Hausser and Vahle curve by numbers inversely proportional to the corresponding wave-lengths. As the actinometric reaction, Dorcas and Forbes selected the photolysis of *p*-benzoquinone in 50-per cent alcohol, a reaction which absorbs completely the light transmitted by the filter. This reaction, which had been studied by P. A. Leighton, satisfies the necessary condition of having a practically constant quantum yield (See Chapter 12) between 3130 and 2540Å. Each wave-length transmitted through the filter may be assumed to photolyze a mass of quinone proportional to the erythema-producing power of the corresponding light component of the original source. The irradiation period was two hours. A second sample was kept in a dark vessel for the same period as control. Both samples were then cooled in ice, and titrated simultaneously with 0.004*N* thiosulfate, adding 10 cc. of normal iodide and of 1.5 normal hydrochloric acid at the start, with starch indicator. It was assumed that all of the monochromatic effects for this reaction could be integrated by summation since the reaction has no induction period and only a few per cent of the reaction material is decomposed, so that absorption by reaction products does not interfere. A plot of the milligrams of quinone decomposed per hour by a series of differently cored carbon arcs against the reciprocals of the times required for the production of a standard erythema indicated a fair degree of proportionality. As such proportionality implies that the reciprocity law holds for both reactions (erythema and photolysis), the slight variations from proportionality involving a

⁸⁰ Stoll, B., *Helv. Phys. Acta*, **8**, 3 (1935); Locher, G. L., *Phys. Rev.*, **42**, 525 (1932); Audubert, R., and Reithmüller, C., *Compt. rend.*, **200**, 389 (1935); Karev, M., and Rodionov, S., *Z. Physik*, **92**, 615 (1934); Audubert, R., and Mattler, J., *Compt. rend.*, **206**, 1005 (1938).

⁸¹ Eidinow, A., *Lancet*, **209**, No. 5320 (1925).

⁸² Dorcas, M. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **49**, 3081 (1927).

⁸³ Hausser, K. W., and Vahle, W., *Strahlentherapie*, **13** (1923); see Chapter 36.

threshold intensity indicate that the reciprocity law does not hold exactly for the erythema reaction.

There had been many attempts to devise methods of chemical actinometry, usually with the object of measuring the value of a source for producing erythema, but rarely had the physical principles underlying the method been analyzed with such thoroughness. Filters were rarely applied (or were used only in a relatively crude manner) and reliance was placed instead upon the choice of a reaction which might be effected within the same wave-length range as that of the reaction to be studied, if, indeed, any consideration at all was given to the matter. The absorption curve of the actinometer was usually taken as an index to the wave-length region within which it is photochemically effected. Variations in the efficiency of the monochromatic rays within the absorbed band were disregarded, and the possibility of the occurrence of side reactions were not always eliminated.

Kistiakowsky and Heidt³⁴ point out that, although the errors of radiometric measurements can be estimated only by the original investigator, many difficulties may be avoided by the proper use of actinometry, and that, if later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it. They describe in detail an apparatus whereby the quantum yield of a photochemical gas reaction over any time interval during its course may be stated in terms of the quantum yield of uranyl oxalate decomposed by monochromatic light of the same wave-length with a probable error of 5 per cent.

Gillam and Morton,³⁵ among the earlier writers on actinometry, proposed the photochemical reduction of potassium nitrate to nitrite (determined colorimetrically) as an index of the bactericidal activity of a source. The absorption of light by nitrates commences at 3300A, rises to a maximum at 3000A, falls to a minimum at 2650 and rises very rapidly beyond this point. The quantum efficiencies below 2860A are, however, much greater than those in the region of selective absorption, so that despite the dissimilarity in absorption of potassium nitrate and bacteria, the photolysis in solutions buffered to pH 9.4 was held to resemble the bactericidal reaction in respect to the spectral distribution of photochemical efficiency.

By this method Gillam and Morton found that an unused mercury lamp gave nitrite equal to 6.4 cc. of N/5000 nitrite, while a used mercury lamp gave only 1.6 cc. An iron-nickel arc produced 5.2 cc. in one hour at 6 inches, or 1.3 cc. at 12 inches, so that the old mercury lamp and the metal arc were effective to roughly the same extent. A test showed that about 98 per cent of the nitrite formed by exposure to the unfiltered lamp owed its origin to rays on the short-wave side of the limiting ray (2750A) transmitted by 0.090 inch of a Vitaglass filter. This was held to indicate that the unfiltered reaction is applicable for measuring the relative bactericidal efficiency of different light sources. The unfiltered reaction is also suitable for indicating the deterioration of a quartz lamp since this deterioration begins in the short-wave region to which the nitrate photolysis is sensitive. The reaction is, however, too slow for general use as a routine test for dosage in actinotherapy. It has been employed by Kestner³⁶ in comparing various ultraviolet sources.

Webster, Hill and Eidinow³⁷ found the bleaching of a solution of methylene-

³⁴ Kistiakowsky, G. B., and Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 3246 (1932).

³⁵ Gillam, A. E., and Morton, R. A., *J. Soc. Chem. Ind.*, **46**, 417 (1927); see Chapter 20 for further discussion of the reaction.

³⁶ Kestner, O., *Strahlentherapie*, **46**, 574 (1933).

³⁷ Webster, T., Hill, L., and Eidinow, A., *Lancet*, **1924**, (1) 745.

blue in aqueous acetone to provide some guide to dosage in actinotherapy. The decomposition products of the acetone effect a bleaching of the dye which is proportional to the time of exposure, the dye evidently acting as a hydrogen acceptor.

Gillam and Morton³⁸ found by the use of filters that about 88 per cent of the acetone-methylene blue reaction is due to rays between 2000 and 2800A, 6 per cent to rays between 2800 and 3250A, and 6 per cent to rays on the long-wave side of 3250A. This indicates that the test is unsuitable as a criterion for the exposures required to effect the conversion of sterols to vitamin D (Chapter 39). On the other hand, it might serve as a simple means of determining dosages in bactericidal experiments. Moss and Knapp³⁹ criticized the test as lacking delicacy.

With mercury-vapor lamps at short distances the acetone-methylene blue test is fairly rapid. It is rather slow in sunlight, but for recording the ultraviolet intensity over a whole day this is an advantage. Exclusion of air is essential for securing reproducible results by this method.⁴⁰

The uranium-sensitized decomposition of oxalic acid was employed by Freer and Gibbs⁴¹ in studying solar radiation in the tropics and was applied to the determination of the intensities of the radiations from the mercury vapor arc by Mathews and Dewey.⁴² The test was standardized for actinometry by Anderson and Robinson,⁴³ Leighton and Forbes,⁴⁴ and by Forbes, Kistiakowsky and Heidt.⁴⁵

The spectrum of an oxalic acid-uranyl salt solution exhibits considerable absorption in the region between 3000 and 3800A. In agreement with this were the experiments of Gillam and Morton with filters of Vitaglass and window glass and a mercury arc, which indicated that 25-30 per cent of the decomposition of the oxalic acid-uranyl salt is due to rays on the long-wave side of 3250A and about 40 per cent to rays longer than 2800A. The region 2700 to 3250A appeared to account for about 20 per cent of the change. With the change induced by sunlight taken as 100, that through 0.09 inch of Vitaglass was 86.7, and through 0.105 inch window glass, 67.5. The test appears to indicate in a very rough way the intensity of those radiations effective in producing erythema. Moss and Knapp⁴⁶ thought the test to be a measure of the rather indefinite dye fading power of a lamp. 4 mm. of Pyrex transmits 40 per cent, 8.2 mm. of clear Corex 70 per cent and red purple Corex (10.2 mm.), 19 per cent of the total radiation as measured by this method.⁴⁷ Erythema on the upper arm is said to be produced by the same quantity of radiation which decomposes 0.056 mg. of oxalic acid per square centimeter in three minutes under standard conditions.

The "Uroxameter" of Moss and Knapp⁴⁸ is an elaboration of this test, using a specially designed vessel (made by Baird and Tatlock) rotated during irradiation of thirty minutes at a distance of 6.5 inches. The test solution consisted of a

³⁸ Gillam, A. E., and Morton, R. A., *J. Soc. Chem. Ind.*, **46**, 417 (1927).

³⁹ Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453 (1925).

⁴⁰ Osborn, T. W. B., and Stammers, A. D., *Brit. J. Actinotherapy*, **5**, 68 (1930).

⁴¹ Freer, P. C., and Gibbs, H. D., *J. Phys. Chem.*, **16**, 709 (1912).

⁴² Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, **17**, 211 (1913).

⁴³ Anderson, W. T., Jr., and Robinson, F. W., *J. Am. Chem. Soc.*, **47**, 718 (1925).

⁴⁴ Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930). In this paper the limitations of actinometry in polychromatic light are discussed.

⁴⁵ Forbes, G. S., Kistiakowsky, G. B., and Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 3246 (1932). For a discussion of the reaction, see Chapter 24.

⁴⁶ Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925).

⁴⁷ Atkins, W. R. G., and Poole, H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929); *Brit. Chem. Abs.*, **A**, 1249 (1929).

⁴⁸ Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925); *Brit. J. Actinotherapy* (Jan., 1927).

mixture of 20 cc. of a 2-per cent aqueous solution of oxalic acid, 5 cc. of a 1-per cent solution of uranyl acetate in water, and 20 cc. of distilled water. For use with carbon arcs, an alternative stock solution richer in uranyl salt was recommended, and called the "20-strength" solution, since with it the distance of irradiation had to be greatly increased. The 20-strength solution was rather unstable, and had, according to Gillam and Morton, a somewhat different absorption spectrum than the normal mixture. Use of the stronger solution increases somewhat the values obtained through Vitaglass from a given source, the K.B.B. lamp. It was reported that a thickness of 2.2 mm. of the reacting solution absorbs all rays shorter than 3210A⁴⁹ and the method was said to indicate sensitivity to the region 3200-2300A. Brackett and Forbes⁵⁰ determined the gross quantum yields (see Chapter 12) at 21°C. (expressed as moles of oxalic acid per quantum) in a solution in which uranyl sulfate is 0.01 and oxalic acid 0.05 molar. The yields are 0.48 ± 0.01 at 2080A, 0.63 ± 0.03 at 2530A, and 0.59 ± 0.01 at 2780A. Forbes and Heidt⁵¹ used uranyl oxalate rather than sulfate (.005 mole) and oxalic acid (.0025 mole) per liter. According to Pitzer, Gordon and Wilson⁵² the rate of reduction of uranyl ion is small until just enough oxalic acid remains to form uranyl oxalate, when the rate of reduction rapidly increases. The presence of sulfuric acid has no effect on the relative rates. The photolyte in the actinometer is a complex, $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{UO}_2\text{C}_2\text{O}_4$ which ionizes as a strong dibasic acid.

The hydrolysis of monochloroacetic acid has also been employed in actinometry.⁵³ Bagnall⁵⁴ reports that the amount of iodine liberated from a solution of potassium iodide acidified with sulfuric acid is a measure of the chemical activity of sunlight and Rousseau⁵⁵ used this reaction in testing the permeability of various substances to the ultraviolet. Moss and Knapp⁵⁶ suggested that the reaction should be carried out in quartz vessels. They also pointed out that unless one unit of ultraviolet radiation liberates the same quantity of iodine from the nearly colorless potassium iodide solution as from the orange-colored mixture of solutions of iodine and potassium iodide, the quantity of iodine liberated will not be directly proportional to the amount of ultraviolet radiation incident upon the solution. Hymas⁵⁷ finds that for periods less than ten minutes, the amount of reaction is proportional to the energy absorbed. The potassium iodide-starch method has a temperature coefficient between 25° and 62°C. of -1.042 for ten degrees. He also finds the deterioration of a mercury lamp to be apparently greater when tested by its action upon potassium iodide than by its action upon sensitized oxalic acid.

From their studies of various methods, Gillam and Morton concluded that the nitrate and carbon tetrachloride methods are most suited to measure the bactericidal rays, while the three oxalic acid methods are more suitable for measuring the "middle ultraviolet."

Clark⁵⁸ employs the rate of darkening of zinc sulfide as a measure of ultraviolet intensity. Zinc sulfide and lithopone are sensitive from about 2500A to about 3600A,

⁴⁹ Moss, J. E., and Knapp, A. W., *Brit. J. Actinotherapy*, May, 1927.

⁵⁰ Brackett, F. P., Jr., and Forbes, G. S., *J. Am. Chem. Soc.*, **55**, 4459 (1933).

⁵¹ Forbes, G. S., and Heidt, L. J., *J. Am. Chem. Soc.*, **56**, 2363 (1934).

⁵² Pitzer, E. C., Gordon, N. E., and Wilson, D. A., *J. Am. Chem. Soc.*, **58**, 67 (1936).

⁵³ Dain, B., and Puzenkin, E., *Ber. Ukrain. wiss. Forsch. physikal. Chem.*, **4**, 75 (1935); *Brit. Chem. Abs.*, **A**, 1211 (1935); *Chem. Abs.*, **29**, 2451 (1935).

⁵⁴ Bagnall, H. H., *Analyst*, **54**, 101 (1929).

⁵⁵ Rousseau, E., *Compt. rend. soc. biol.*, **93**, 1480, 1482 (1925).

⁵⁶ Moss, J. E., and Knapp, A. W., *Analyst*, **54**, 334 (1929).

⁵⁷ Hymas, F. C., *Quart. J. Pharm.*, **2**, 281 (1929).

⁵⁸ Clark, J., *Am. J. Physiol.*, **69**, 900 (1924); *Am. J. Hygiene*, **9**, 646 (1929); *J. Opt. Soc. Am.*, **21**, 240 (1931).

with a maximum darkening at about 3200Å. Mayerson⁵⁹ finds the method satisfactory if the change in reflection factor is measured. For measuring solar ultra-violet radiation, he finds the acetone-methylene blue the least applicable and the oxalic acid-uranyl sulfate reaction the most useful of these three methods. He presents a comparison of the data obtained by other workers with these methods, recalculated to absolute units.

Eisenschimmel⁶⁰ suggested the diminution of the active chlorine content of chloramine-T in 0.2N solution in methanol as a measure of the intensity of actinic light. The reaction was carried out in glass test tubes. No information as to the effective wave-lengths is available.

Weyde and Frankenburger⁶¹ measure the erythema-producing region of the ultraviolet by the photochemical formation of crystal violet in an alcoholic solution of its leucocyanide or sulfite. For radiations of 3130Å and 2537Å, the quantum efficiency is one. A small quantity of potassium cyanide or sulfite is added to the alcohol solution. By using sufficiently thick layers of solution, it is possible to measure 10^{15} dye molecules, corresponding to 6.8×10^8 ergs. For ultra violet intensities of one erg per square centimeter, the exposure is one hour. Harris and Kaminsky⁶² report that photolysis of crystal violet leucocyanide or sulfite is less desirable than photolysis of methylene-green leucocyanide for which the Einstein equivalence law (Chapter 12) holds with an accuracy of 2.5 per cent in absolute value and an average precision of 1.4 per cent for three wave-lengths. The latter reaction is said to be especially adapted for the measurement of very small light energies.

Anderson and Bird⁶³ used a fluorescence photometer with different chemical substances to measure the relative intensities of monochromatic ultraviolet light throughout the spectrum, and found that they could check the intensities as given by a thermopile. It was concluded that the photometric method may be employed for measuring accurately the ultraviolet energy.⁶⁴ Although fluorometers are simple and inexpensive,⁶⁵ Forbes⁶⁶ does not regard them as very precise.

Athanasiu⁶⁷ investigated the effects of light on voltaic cells. The latter were described as electrochemical actinometers. The maximum sensitivity of actinometers having electrodes of mercury salts in contact with 10 per cent sulfuric acid is at 2536Å for mercurous chloride and at 2967 for mercurous bromide. The chloride and bromide are sensitive only to the ultraviolet; they are fluorescent under the latter, emitting a strong visible radiation. The effects were too great to be photoelectric and were attributed to photochemical changes at the surfaces of electrode-producing films. There are, in addition to an electrolyte, two similar metallic electrodes, one kept dark and the other irradiated. Polarization and thermal effects also play a part. With copper electrodes in copper sulfate, an

⁵⁹ Mayerson, H. S., *Am. J. Hyg.*, **22**, 106 (1935).

⁶⁰ Eisenschimmel, W., *Z. Zuckerind. Cechoslov. Rep.*, **51**, 535 (1927), *Chem. Abs.*, **22**, 356 (1928). The rate of combination of hydrogen and chlorine has been proposed as a measure of light intensity by C. Chilowsky, *British P.* 463,994, April 9, 1937, and 469,636, July 29, 1937; *Chem. Abs.*, **32**, 429 (1938).

⁶¹ Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1932); U. S. P. 1,845,835, Feb. 16, 1932, of Frankenburger, W., Rohl, R., and Zimmermann W.; *Naturwiss.*, **18**, 206 (1930); *Chem. Abs.*, **26**, 2121 (1932). Diazo compounds have also been employed in actinometers. N. V. Chemische Fabrik, L. van der Grinten, *French P.* 820,108, Nov. 4, 1937; *Chem. Abs.*, **32**, 5307 (1938).

⁶² Harris, L., and Kaminsky, J., *J. Am. Chem. Soc.*, **57**, 1154 (1935).

⁶³ Anderson, W. T., Jr., and Bird, L. F., *Phys. Rev.*, **32**, 293 (1928).

⁶⁴ See also Croad, A. K., *British P.* 320,794 (1928).

⁶⁵ Winther, C., *Z. Elektrochem.*, **19**, 390 (1913); Gycmant, A., *J. Opt. Soc. Am.*, **12**, 65 (1926).

⁶⁶ Forbes, G. S., *J. Phys. Chem.*, **32**, 488 (1928).

⁶⁷ Athanasiu, G., *Compt. rend.*, **180**, 587 (1925); *J. Soc. Chem. Ind.*, 689A (1922); *Ann. Physique*, **4**, 318 (1925).

E.M.F. of the order of 40 millivolts can be obtained, the irradiated electrode being negative.⁶⁸

Intensities of Various Lines as Related to Their Origins. The physical techniques described above have been applied to studies of the intensities of various lines and the results interpreted in terms of the probabilities of the occurrences of the corresponding transitions between energy states. These will not be discussed since the photochemist is more concerned with the broader features of the energy distribution of the spectral intensities within the various wave-lengths regions than with the physical theory of the intensities of individual lines.

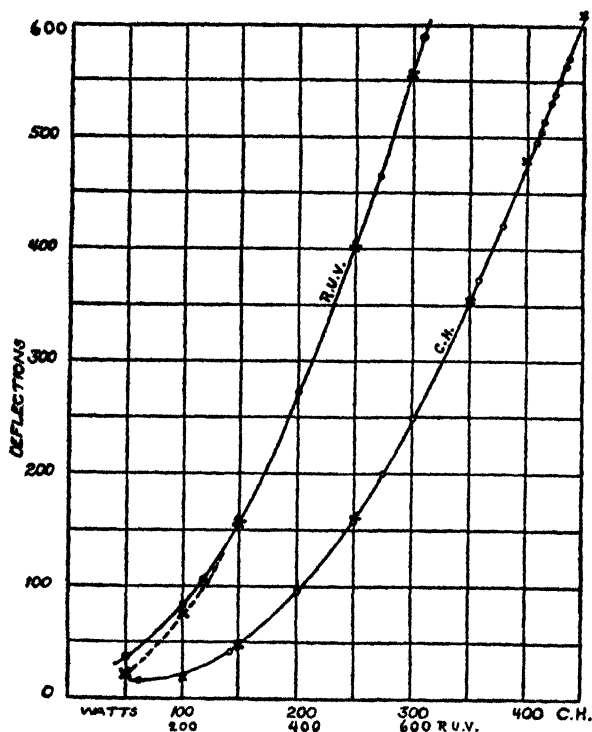


FIGURE 45. Variation in Total Radiation Emitted with Variation in Power Input (Coblentz, Long and Kahler, *Bureau of Standards Scientific Papers*).

DATA ON THE OUTPUT AND SPECTRAL DISTRIBUTION OF QUARTZ MERCURY ARCS

Hulburt⁶⁹ found the total radiation from 6000 to 2300Å from a quartz mercury lamp as measured with a thermocouple to be 1.54×10^8 ergs per second. This would be equivalent to about 50 quanta emitted per mercury atom per second were all the energy at 5000Å. Küch and Retschinsky⁷⁰ studied the spectral distribution

⁶⁸ See also Imori, S., and Takebe, T., *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, 8, 131 (1928).

⁶⁹ Hulburt, E. O., *Phys. Rev.*, 31, 1109 (1928); 32, 593 (1928).

⁷⁰ Küch, R., and Retschinsky, T., *Ann. Physik*, 20, 563 (1906); 22, 595 (1907); see also Pflüger, *Ibid.*, 26, 789 (1908); Athanasiu, G., *Compt. rend.*, 178, 2071 (1924); Shoda, M., *Japan. J. Physics*, 9, 27 (1934); *Chem. Abs.*, 28, 4310 (1934); Koch, B., *Ann. Physik*, 33, 335 (1939).

of the energy from mercury arcs. They determined the total visible intensity and the intensities of individual visible lines by a flicker photometer, the ultraviolet by a photoelectric cell, and the continuous background by a photographic method. They also investigated absorption by mercury within the lamp.⁷¹ Other early determinations of the energy distribution of this source were made by Ladenburg,⁷² Hallwachs,⁷³ Fabry and Buisson,⁷⁴ Winther,⁷⁵ Allmand,⁷⁶ Souder,⁷⁷ Coblenz, Long and Kahler,⁷⁸ and Coblenz and Kahler.⁷⁹

Coblenz, Long and Kahler give the variation of energy of wave-lengths less than 1.4μ as affected by variations in power input for a Cooper-Hewitt and an R.U.V. lamp. (Figure 45.) The experimental curves are closely represented by the formula $E = KW^x$, where for one lamp $K = 0.00462$ and $x = 1.83$ and for the other $K = 0.000457$ and $x = 2.314$.

Reeve⁸⁰ pointed out that the early work could not be used for a calculation of the absolute amount of energy emitted at any particular wave-length. He gave an intensity wave-length diagram for a 100-hour old Cooper-Hewitt 110-volt lamp operated at 62 volts and 4.2 amperes. In his diagram each "line" was given a triangular form, the base of the triangle being the wave-length region included. This method was adopted since the monochromator slit employed transmitted a finite range of wave-lengths rather than just the line width. Reflection and absorption losses, and the influence of compound lines, were considered.⁸¹ For the relative energies of the mercury lines expressed in arbitrary units, he found the values given in Table 2.

Table 2.—Relative Energy of Mercury Lines.

Wave-length	Intensity	Wave-length	Intensity
248.5 m μ	7.1	303 m μ	82.5
254	39.5	313.5	213.0
265.5	35.1	334	9.4
270	6.6	366.5	326.0
275	2.3	406.5	111.4
280.5	20.3	437.5	166.6
290	17.9	559.	189.0
297	32.7	585.	207.

The early works contained some discrepancies in the ratios of the intensities of various lines. For example, Pfüger found that of the yellow line to the green line to be 140 to 90, while Ladenburg gave it as 27.4 to 42.9. The source of this and other discrepancies was attributed by Reeve to the influence upon the relative intensities of various lines of the electrical conditions, dimensions and age of the lamp.

A standard type commercial lamp run on 2.2 amperes and 10 volts per centimeter will deliver at an exit slit 40×1 mm. of a monochromator with 50 mm. objectives

⁷¹ Küch, R., and Retschinsky, T., *Ann. Physik*, 22, 852 (1907).

⁷² Ladenburg, E., *Physik. Z.*, 5, 525 (1904).

⁷³ Hallwachs, W., *Ann. Physik*, 30, 593 (1909).

⁷⁴ Fabry, C., and Buisson, H., *Compt. rend.*, 153, 93 (1911).

⁷⁵ Winther, C., *Z. Elektrochem.*, 20, 109 (1914).

⁷⁶ Allmand, A. J., *J. Chem. Soc. Trans.*, 107, 682 (1915).

⁷⁷ Souder, W. H., *Phys. Rev.*, 8, 316 (1916).

⁷⁸ Coblenz, W. W., Long, M. B., and Kahler, H., *Bur. Standards Sci. Paper*, No. 330 (1918).

⁷⁹ Coblenz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920).

⁸⁰ Coblenz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920); see also Boll, M., *Compt. rend.*, 156, 313 (1913); *J. Chem. Soc.*, 104, 182 (1913).

⁸¹ Reeve, L., *J. Phys. Chem.*, 29, 39 (1925).

⁸² Franklin, R., Maddison, R., and Reeve, L., *Ibid.*, 29, 713 (1925).

and an aperture ratio 4.5, 8×10^8 ergs per second at 3660Å and 4×10^2 ergs per second at 2800Å, where the energy of a quantum is nearly a third greater.⁸²

Beesley and Ridyard⁸³ recorded the energy distribution of a Uviol lamp burning at 29.5 volts and 2.42 amperes, and compared it with the data previously obtained by Allmand,⁸⁴ as well as with the energy distribution of the quartz mercury lamp. Their data are not included here as this lamp is now rarely used in photochemical work.

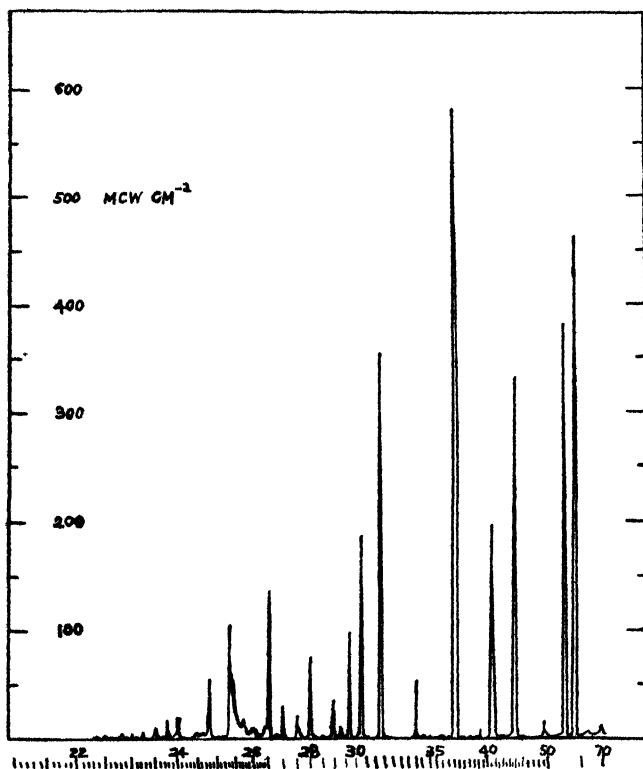


FIGURE 46. (McAlister, *Smithsonian Miscellaneous Collections*.)

Atkins and Poole⁸⁵ compared photochemical and photoelectric measurements of the radiation from a mercury vapor lamp. Andant and Lecompte⁸⁶ recorded the relative intensities of the principal lines from the yellow doublet to 2536Å emitted by mercury vapor lamps of various designs functioning under different conditions. For the same arc, the intensity of emitted radiation changes greatly with the arrangement of the apparatus, especially with the voltage at the terminals. For two different arcs and for the same spectral line, an identical variation in each lamp does not produce the same effect on the emission.

⁸² Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2449 (1925).

⁸³ Beesley, E., and Ridyard, H. N., *J. Phys. Chem.*, **32**, 1342 (1928).

⁸⁴ Allmand, A. J., *J. Chem. Soc.*, **107**, 682 (1915).

⁸⁵ Atkins, W. R. G., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929).

⁸⁶ Andant, A., and Lecompte, J., *J. Phys. Radium*, **1**, 65 (1930).

The relative intensities of prominent lines in the ultraviolet have been studied by Coblentz, Stair and Hague.⁸⁷ Absolute intensities in the visible and ultraviolet ranges have been recorded by McAlister.⁸⁸ In Figure 46 are given the intensities of 32 lines at 250 mm. from a 20 mm. midsection of a 400-hour-old Cooper-Hewitt direct current arc operated at high intensity (4.5 amperes and 150 volts). These values, expressed in microwatts per square centimeter may be multiplied by 7.1 to obtain approximate values for the full length of the arc exposed. Figure 47 gives similar data for the same arc operated at low intensity (3.0 amperes and 44 volts).

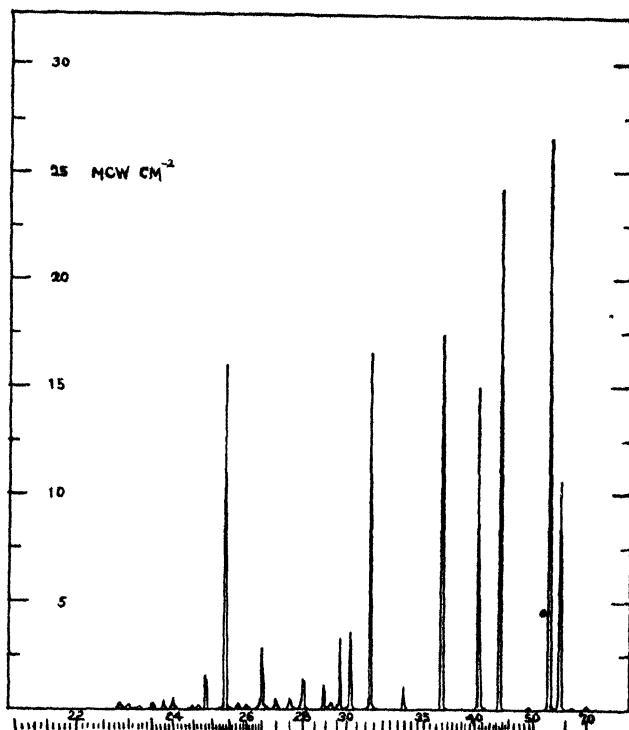


FIGURE 47. (McAlister, *Smithsonian Miscellaneous Collections*.)

In the former case the vapor pressure of the mercury is approximately atmospheric; in the latter it is but a few millimeters. Microphotometer curves of spectrograms in the region of the resonance line (Figure 48) show that even under low intensity conditions, the resonance line is partly reversed by absorption by mercury vapor, and that at high intensity conditions it is completely absorbed.⁸⁹ The mercury arc

⁸⁷ Coblentz, W. W., Stair, R., and Hague, J. M., *Bur. Standards J. Research*, **8**, 760 (1932).

⁸⁸ McAlister, E. D., *Smithsonian Miscellaneous Collections*, **87**, No. 17 (1933).

⁸⁹ Wood, R. W., [*Phil. Mag.*, **23**, 689 (1912)] found mercury vapor to absorb its resonance line so strongly that a quartz bulb filled with mercury vapor at room temperature (vapor pressure 0.001 mm.) casts a shadow when illuminated by this line alone. A thickness of 0.5 mm. reduces the intensity to one-third its initial value. This is not the only line absorbed by mercury vapor under arc conditions. Crew, W. H., and Dawson, L. H., [*J. Opt. Soc. Am.*, **17**, 261 (1928)] found some thirteen lines, including two "spark lines" to show self-reversal. For further studies, see Hughes, A., and Thomas, A., *Phys. Rev.*, **30**, 466 (1927); Mohler, F. L., and Moore, H. R., *J. Opt. Soc. Am.*, **15**, 74 (1927); Kopfermann, H., and Tietze, W., *Z. Physik*, **56**, 604 (1929).

usually employed apparently does not emit this resonance line. In the high intensity arc, the energy in this region is all due to the neighboring 2534.8A line and to the continuous background. Four different arcs showed differences averaging 5 per cent for some lines, the maximum being 10 per cent for the 2537A line.

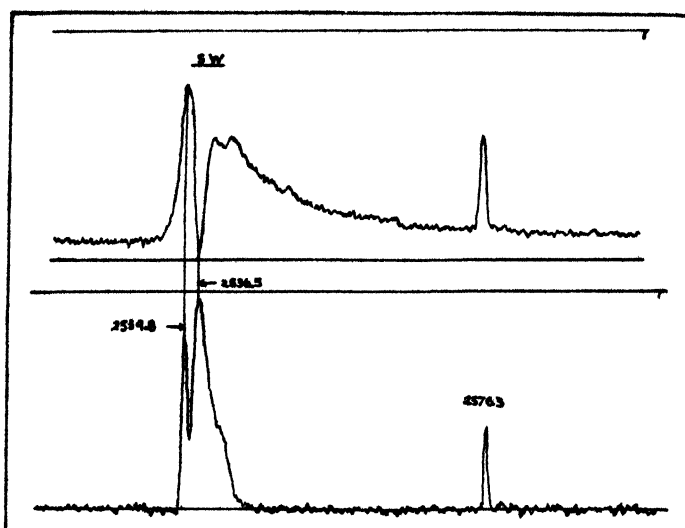


FIGURE 48. Microphotometer Curves in the Region of the Resonance Line (From McAlister, *Smithsonian Miscellaneous Collections*).

Observations made with the aid of filters (Table 3) showed the distribution of energy into various regions.

Table 3.—Distribution of Energy for Mercury Arcs.

		1 0.2-0.35 μ	2 .35-1.4 μ	3 1.4-19 μ	4 >19 μ	5 Total
<i>High Intensity.</i>						
20 mm. of vertical arc	mcw. cm. ⁻²	84	167	245	68	564
	per cent	14.8	29.7	43.4	12.1	100
Total vertical arc	mcw. cm. ⁻²	600	1130	2710	350	4700
	per cent	12.5	23.6	56.6	7.3	100
Total horizontal arc	mcw. cm. ⁻²	615	995	2700	370	4680
	per cent	13.2	21.2	57.7	7.9	100
<i>Low Intensity.</i>						
20 mm. of vertical arc	per cent	3.0	8.0	81.7	8.3	100
	mcw. cm. ⁻²	2.8	7.7	77.5	8.0	96
Total vertical arc	mcw. cm. ⁻²	19.8	59.6	704.8	124.	908.
	per cent	2.3	6.6	77.6	13.5	100.

Forsythe, Barnes and Easley⁹⁰ have compared the intensities, distribution, and output of ultraviolet radiation from the quartz mercury arc and several types of

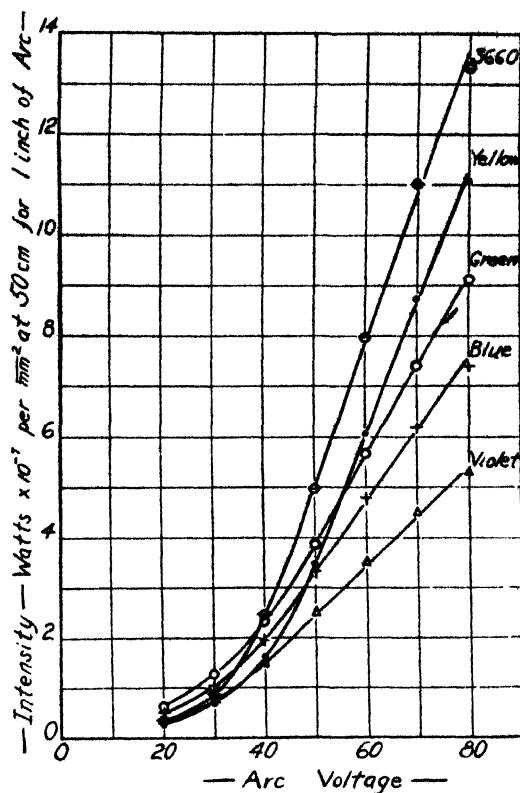
⁹⁰ Forsythe, W. E., Barnes, B. T., and Easley, M. A., *J. Opt. Soc. Am.*, 21, 30 (1931); 24, 178 (1934).

"sun lamp" (see Chapter 8), and Waguet⁹¹ has studied the light emission of mercury arcs at high pressure. Other relative data, obtained with a spectrometer and thermopile with galvanometer, were given by Oguri.⁹²

It has been shown⁹³ that the spectrum of the light from a given mercury arc varies in character and intensity with the part of the lamp from which the light is emitted. The variation occurs because of irregularities in the thickness and curvature of the quartz envelope. For accurate spectrographic work, this source of error may be remedied by inserting a plane quartz window in the side of the burner.

FIGURE 49.

Effect of Arc Voltage on Intensities of Line Groups (Johnson and Burns, *Journal Optical Society of America*).



Absolute line intensity and energy distribution data in high and low-pressure arcs were obtained by Johnson and Burns,⁹⁴ employing a method of photographic photometry (using as comparison a standardized mercury arc) developed by Stockbarger and Johnson. In this method, characteristic curves for the plates were taken for each line measured. Variations of the line intensity with current or voltage were measured on a quartz radiometer, and converted into absolute units by com-

⁹¹ Waguet, P., *Compt. rend.*, 201, 450 (1935). See also Kern, J., *Z. tech. Physic*, 19, 249 (1938); *Chem. Abs.*, 32, 8929 (1938), and Larché, K., and Rössler, F., *Physik. Z.*, 37, 800 (1936); *Chem. Abs.*, 31, 6549 (1937).

⁹² Oguri, S., *J. Chem. Ind. (Japan)*, 38, Suppl. binding, 392 (1935); 39, 35, 143 (1936); *Brit. Chem. Abs.*, B, 635 (1936).

⁹³ Takahaashi, T., and Clark, L. H., *J. Sci. Instruments*, 6, 273 (1929).

⁹⁴ Johnson, L. B., and Burns, L., *J. Opt. Soc. Am.*, 23, 55 (1933).

parison with the absolute values determined by photographic photometry at one current and voltage.

The vertical type high-pressure arc had an arc length of three inches. The current was kept at 4 amperes by a hand-controlled rheostat and the voltage was maintained at 45 volts by a voltmeter, photoelectric cell and an amplifier so arranged as

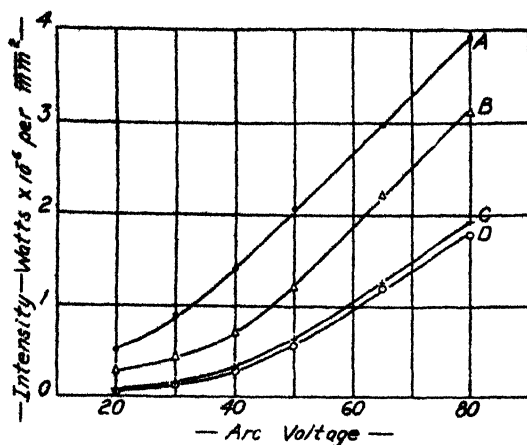


FIGURE 50.

Effect of Arc Voltage on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

to control the voltage through the temperature by regulating a blast of air on the cathode of the arc. Table 4 gives the intensities of the visible and near ultraviolet lines. The low pressure arc was 22 inches long and was operated at 4 amperes and approximately 37 volts.

Table 4.—Intensities of Visible and Near-Ultraviolet Lines.

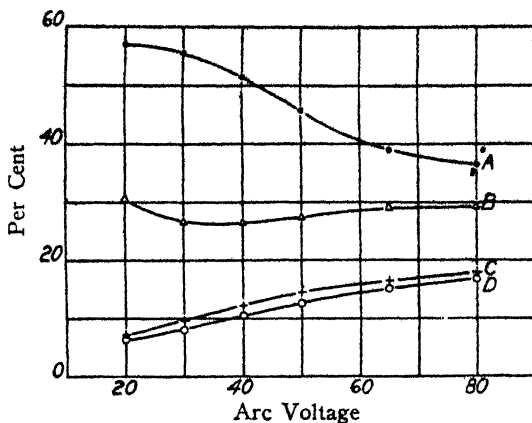
Group	Line	Intensity (watts $\times 10^{-6}$ /mm ² at 50 cm. for 1 inch of arc)	
		High-pressure arc	Low-pressure arc
Yellow	{ 5791A	0.102	0.009
	{ 5770	0.124	0.010
Green	5461	0.305	0.057
Blue	{ 4358	0.232	0.053
	{ 4348	0.014	0.0008
	{ 4339	0.006	0.0003
Violet	{ 4078	0.022	0.0058
	{ 4047	0.170	0.042
3660	{ 3663	0.075	0.0068
	{ 3655	0.086	0.0075
	{ 3650	0.190	0.0126

Figure 49 shows the variation of the intensities of the line groups with arc voltage for the high-pressure arc carrying 4 amperes. The results confirm the data of earlier workers that lines of the same series (5461, 4358 and 4047, which give most of the radiation in their groups) increase in intensity together and retain their intensity ratios.

By the use of filters, the total radiation was divided into four regions (A, 14,000-40,000A; B, 3800-14,000A; C, 2950-3800A; D, 1850-2950A) and the varia-

FIGURE 51.

Effect of Arc Voltage on Relative Output in Various Regions (Johnson and Burns, *Journal Optical Society of America*).



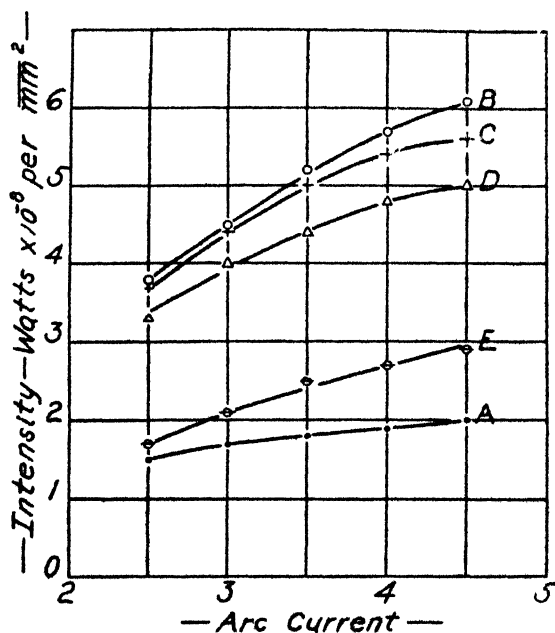
tions of the intensities of each with arc voltage are shown in Figure 50. The total radiation for the whole arc, including the electrodes, was determined in microwatts per square mm. at 50 cm. The variation of intensity with the voltage is shown in Table 5.

Table 5.—Variation of Intensity with Arc Voltage

Arc voltage	80	70	60	50	40	30	20
Intensity	10.74	8.60	6.50	4.43	2.72	1.57	0.888

FIGURE 52.

Effect of Current on Intensities of Line Groups (Low-pressure Arc) (Johnson and Burns, *Journal Optical Society of America*).



In Figure 51, the results secured are expressed in terms of the variation of the per cent of the total radiation in each of these regions with arc voltage (at 4 amperes).

For the low-pressure arc, the variation of the intensity of the groups of lines of Table 4 with the current at 37 volts, is given in Figure 52. The low-pressure arc was very sensitive to drafts and changes in room temperature. Immediately after a sudden reduction in the arc current, the total intensity went up, but after ten or fifteen minutes came back to approximately the same value. If the arc was running

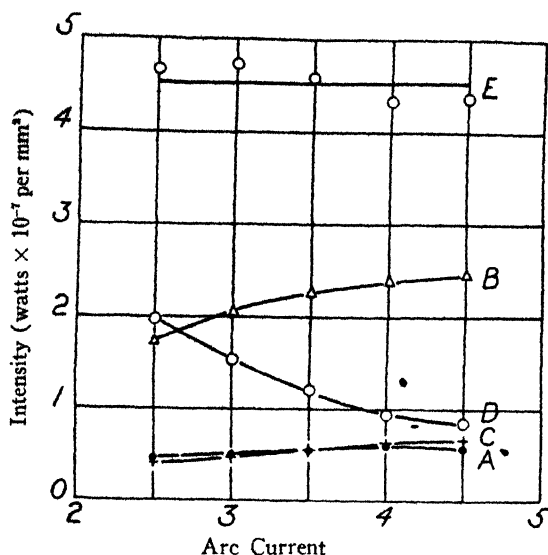


FIGURE 53.

Effect of Current on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

at 40 volts and a blast of air was played upon it, the arc voltage would decrease until a minimum was reached at about 36 volts. At this point, if the arc was further cooled, the voltage would again increase. The line intensity depended on whether the arc was running on the hot or the cold side of the minimum. The data in the figures were obtained on the hot side.

The variations with arc current of the intensities of each of the four regions separated by the filters from five inches of arc are given in Figure 53 along with the total intensity (curve E). The latter is believed to be constant, the variation of the individual points from a horizontal line being ascribed to the sensitivity of the arc to varying ventilation. The effect of variation of the arc current on the energy distribution is given in Table 6. It is important to note that at 2.5 amperes, the

Table 6.—Energy Distribution for Various Arc Currents.

Region	4.5 amp.	4.0 amp.	3.5 amp.	3.0 amp.	2.5 amp.
14000-40000A	12.3%	13.0%	11.9%	11.0%	9.9%
3800-14000A	53.9	52.8	50.0	45.0	37.8
2950-3800A	15.0	13.4	12.0	10.3	8.8
1850-2950A	18.8	20.8	26.1	33.7	43.5

intensity of the far ultraviolet reaches the high value of 43.5 per cent, and it appears likely that at lower currents, still higher percentages may be found, although the arc then becomes very unstable unless there is accurate temperature control of the surrounding air. Johnson and Burns also included data for the low-pressure arc in Uviol glass, and in UV 690 and UV 888 glasses.

Owen and Wright⁹⁵ have considered the effects of the position of the arc upon the spectroscopic analysis of the ultraviolet. Data comparing energy-emission for various artificial sources of ultraviolet radiation have been reported by van Wijk and Reerink,⁹⁶ Greider⁹⁷ and by Krefft and Pirani,⁹⁸ the latter dealing chiefly with sources of infrared rays.

Forbes and Leighton⁹⁹ indicated the complex nature of the factors controlling the intensity of a given line and showed that for any line and current strength, the maximum intensity is proportional to the pressure, the slopes and intercepts varying with the wave-length and internal diameter of the lamp. This relation was true up to five atmospheres in the constricted arc, but in a 9-mm. arc at high pressures the intensity increases less rapidly than the pressure. The latter phenomenon was attributed to the presence of a 3-mm. shell of absorbing vapor.

Harrison and Forbes¹⁰⁰ found that for a given power input, the intensity is much greater for high voltages and pressure and low current than it is for high current and low voltage and pressure. In Table 7 are given for the wave-length regions arbitrarily numbered in column 1 (including the lines in column 2) a rough estimate of the relative intensities of the various components of each group. The measurements were obtained with a spectroradiometer with a silver-bismuth thermopile. No corrections were made for reflection or absorption in the optical train, or for the effective slit-width. Only the relative intensities of single lines were measured.

Table 7.—Relative Intensity of Various Wave-lengths.

Group 1, 2	Wave-lengths selective quartz radiation	Relative Intensity ?	Group 9	Wave-length	Relative Intensity
				3663	4
				3655	6
				3650	10
3	11288A	2			
	10140	5	10	3352	..
				3342	..
4.	6234	1			
	6152	2	11	3132	4
				3126	5
5	5819	3			
	5804	3	12	3026	1
	5790	3		3024	2
	5769	6		3022	2
	5461	5			
			13	2804	1
7	4539	5			
	4348	5	14	2700	2
8	4078	3	15	2537	2
	4047	3			
			16	2438, etc.	1

Also, it was pointed out that the intensity of any line increases linearly (at constant current maintained by varying the ventilation of the arc) as the voltage

⁹⁵ Owen, E. A., and Wright, P., *Brit. J. Radiol.*, **5**, 330 (1932).

⁹⁶ van Wijk, A., and Reerink, E. H., *Physica*, **13**, 289 (1933).

⁹⁷ Greider, C. E., *Ind. Eng. Chem.*, **23**, 508 (1931).

⁹⁸ Krefft, H., and Pirani, M., *Z. tech. Physik*, **14**, 393 (1933).

⁹⁹ Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, **12**, 53 (1926).

¹⁰⁰ Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, **10**, 1 (1925).

gradient is increased beyond a limiting value which varies with the individual line and the current. Table 8 shows for the numbered groups the ratio of the intensities to that of the yellow-green lines (maximum or group five) for various voltages at 2.5 amperes. The energy of the 3660 line was found to be increased 17.1 times by

Table 8.—Relative Intensity of Groups to Yellow-Green Line.

Maximum	Ratio to Maximum Five (Yellow-green Lines)				
	5 Volts	7 Volts	9 Volts	11 Volts	14 Volts
3	0.347	0.337	0.359	0.375	0.402
5	1.000
7	0.725	0.738	0.655	0.600	0.562
8	0.375	0.474	0.407	0.369	0.345
9	0.909	1.100	1.120	1.080	1.050
10	0.587	0.705	0.638	0.545	0.545
12	0.173	0.279	0.303	0.332	0.329
14	0.013	0.147	0.168	0.166	0.165
15	0.013	0.170	0.180	0.171	0.165

a 3.5-fold increase of the voltage gradient (from 4 to 14 volts per centimeter). Also it was stated that at 4.5 amperes and 25 watts per centimeter, only half as much energy will go into the yellow-green maximum as will when the current is 1.5 amperes and the voltage three times as great. For high efficiency, the arc should be cooled as little as possible. The ratio of intensities of any two lines of the same series was essentially constant.

The average arc shows the smallest change in energy distribution for a given variation in total intensity when the pressure is as high as possible. As this is the condition of greatest intensity of all the maxima, the best operating conditions seem to comprise as high a pressure and voltage drop as is consistent with the life of the lamp and with its mechanical structure.

Asada¹⁰¹ proposes for the relation between the light intensity, the current and the potential difference, the expression, $G = kI(V - a)^n$, where G is the light intensity, k a constant, I the current, V the potential, a is a lamp constant determined as the least terminal voltage, and n is a constant for any given wave-length. The relation holds for both alternating-current and direct-current lamps, effective values being used in the former case. The value of n depends upon the type of current used.

Harris¹⁰² found that there is a great outburst of ultraviolet energy from a cold lamp immediately after striking the arc, the current then having a maximal value and the resistance and voltage minimal values. This initial flare is quite evanescent, being followed by a sudden fall to the real onset of the permanent vaporizing and incandescent period. The latter begins after the first minute of arc striking has elapsed.¹⁰³ During the next two minutes, the voltage doubles and the lamp warms up, raising the vapor to incandescence. In the second and third minutes, a precipitous rise in emission occurs, the slope of which can be affected by controlling the temperature of the lamp. A blast of air causes the emission to rise slowly to its final value. A parabolic reflector behind the lamp reduces the rate of cooling on one side, so that incandescence is reached more quickly, but the emission falls again to a level slightly below that of the lamp under normal conditions in still air. For a constant source, the arc with a fan directed upon it, is to be chosen. Under these

¹⁰¹ Asada, T., *J. Elec. Eng. Inst. (Japan)*, 51, 36 (1931); *Chem. Abs.*, 26, 1522 (1932).

¹⁰² Harris, D. T., *Rev. Sci. Instruments*, 6, 2 (1929).

¹⁰³ See also Watters, B. D., *Brit. J. Radiology*, 81, 163 (1924).

conditions, devitrification and discoloration of the quartz is reduced, avoiding the rapid fall in efficiency most marked in the extreme ultraviolet. Figure 54¹⁰⁴ shows in the left half the changes (on starting the Uviarc) which occur in the total energy, energy of the arc and electrodes, and arc alone, the latter only being concerned with the emission of the mercury lines. The right half of the figure shows in heavy lines the effect of cooling the arc on the increase of current, the energy expended in the arc, electrodes and arc and the total watts. In lighter lines are shown the corresponding effect of increasing the series resistance, Maddock¹⁰⁵

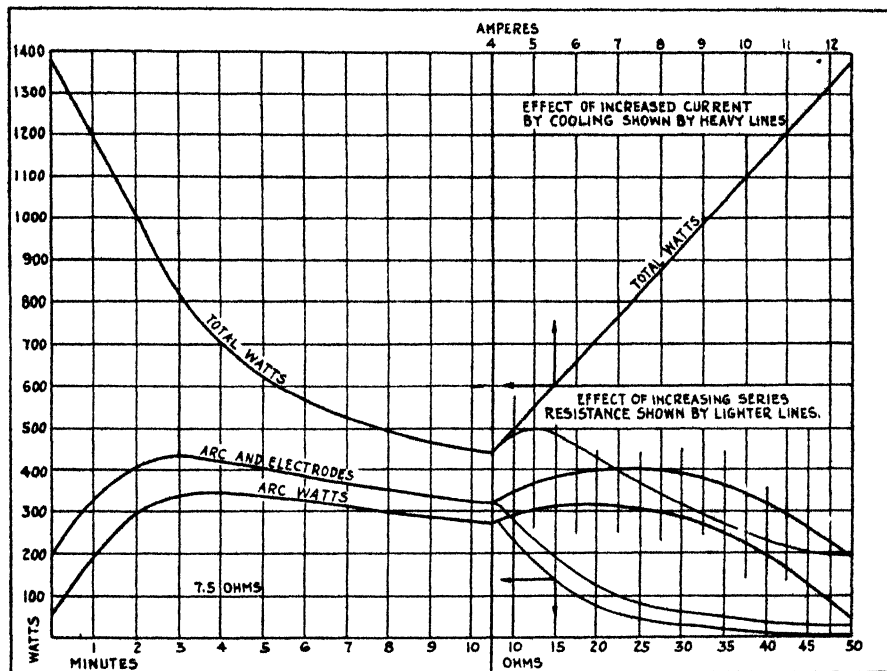


FIGURE 54. Energy Distribution under Various Operating Conditions (Buttolph, *Review Scientific Instruments*).

plotted arc watts—intensity variation curves for temperature variation of the air surrounding the burner, and tabulated absolute intensities for thirty lines between 7000 and 2300Å.

MEANS FOR INCREASING THE OUTPUT OF THE RESONANCE LINE

To issue from the lamp the light of the bright radiant axial thread must first penetrate the envelope of vapor and undergo absorption. To obviate this absorption effect the temperature of the envelope may be reduced thereby lowering the vapor pressure. This can be effected by cooling with water, but owing to condensation of mercury vapor, a coating of mercury may form on the inside wall of the lamp and prevent the issuance of light. Another method of preventing the limita-

¹⁰⁴ Buttolph, L. J., *Rev. Sci. Instruments*, 1, 497 (1930).

¹⁰⁵ Maddock, A. J., *Proc. Phys. Soc. (London)*, 47, 424 (1935).

tion of the output by absorption, used particularly in lamps for the study of resonance phenomena where a strong emission of the resonance line is required, is based upon¹⁰⁶ deflection of the arc toward one side of the tube of the lamp by means of an electromagnet. This operation is said to raise the temperature of the tube at the place where the arc is applied, thus burning an aperture in the film resulting from condensation. The light of the deflected radiating arc will issue through this aperture without having penetrated an absorbing layer of mercury vapor. Figure 55 shows the construction of this apparatus.

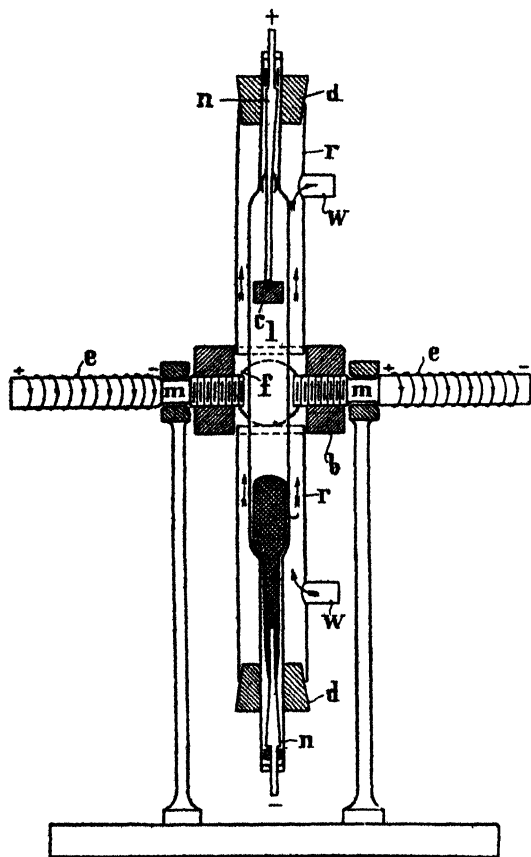


FIGURE 55.

Kerschbaum's Apparatus for Magnetic Deflection of the Mercury-vapor Arc.

The brass block (b) has a vertical bore; into this are soldered two tubes (r) having branches (w) for receiving and discharging the cooling water. Into this vertical cooler is inserted a quartz mercury-vapor lamp (1), which is fastened above and below by means of bored rubber stoppers (d). The quartz lamp is a vertically burning lamp, which is of the simplest and most compact construction possible. As leading-in members for the lamp, ground-in nickel-steel pins (n) serve. Only the metal of the lower electrode (cathode) is mercury. The anode

¹⁰⁶ Kerschbaum, F., U. S. P. 1,118,868, November 24, 1914; *Chem. Abs.*, 8, 2315 (1914).

is a piece of carbon (c) screwed on the end of the upper nickel-steel pin. The brass block (b) has in addition two lateral, horizontal, threaded bores. By means of these apertures the ends of two iron rods (m) are screwed up close to the wall of the lamp; over these rods are pushed coils of wire (e). Each of the two coils has 200 turns of covered copper wire of $\frac{1}{2}$ ohm resistance; the current employed is 2 to 3 amperes. The electromagnets so formed produce lines of force at right angles to the axis of the lamp. The block (b) has another horizontal bore (f). This passes through only the rear half of the block and can be closed by a quartz plate. When the lamp is burning and the electromagnets are so connected that they deflect the arc to the rear, the light will issue through the bore (f) and enclosing

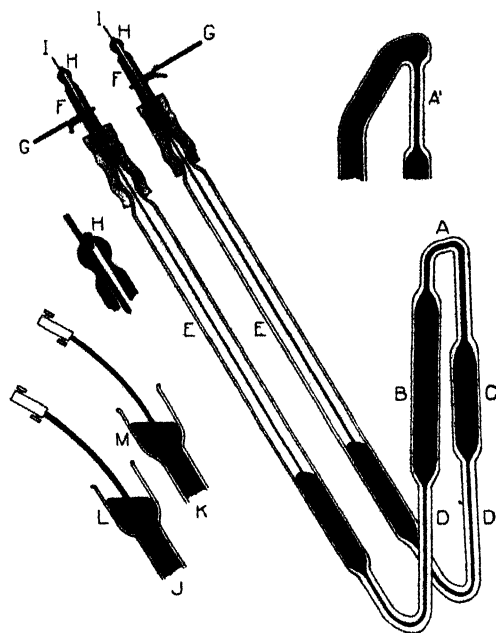


FIGURE 56. Diagram of the constricted arc, arranged for pressures up to five atmospheres and currents from 0.2 to 2.0 amperes. The inserts show at A' the modified form of the constricted portion, arranged to water-cool the hot column so that currents up to 5.0 amperes could be used, and below the enlarged ends arranged for work at atmospheric pressure (Forbes and Harrison, *Journal of the Optical Society of America*).

quartz plate. The arc is drawn by rotating the lamp into its horizontal position. Tanberg¹⁰⁷ has studied the physical phenomena involved in the passage of a mercury arc at low vapor pressure in a magnetic field.

The Constricted Arc. In these arcs the non-luminous portion of the arc is eliminated by making the tube of such narrow diameter that it is practically completely filled by the narrow luminous thread. They are usually laboratory made, and may be operated at pressures up to about 5 atmospheres, but are comparatively short-lived. Harrington¹⁰⁸ described a lamp operated on 25 volts

¹⁰⁷ Tanberg, R., *Nature*, 124, 371 (1929). See also Fabrikant, V. A., and Rokhlin, G., *Compt. rend. acad. sci. U.R.S.S.*, 19, 393 (1938); *Chem. Abs.*, 32, 8256 (1938).

¹⁰⁸ Harrington, E. L., *J. Opt. Soc. Am.*, 7, 689 (1923).

direct current (10 volts per centimeter), yielding a brilliant light of capillary tube dimensions.¹⁰⁹ Vincent and Biggs¹¹⁰ described an arc with a 0.3 mm. column, open to the air and carrying 0.1 to 0.16 ampere at 100-150 volts; it had low current capacity. Harrison and Forbes¹¹¹ designed two special lamps. The first of these (Figure 56) had in A a bent tube 63 mm. long, of 2.0 mm. bore and 7 mm. external diameter. It extended between two mercury reservoirs, one at a higher level than the other. The one at the higher level was made negative, so that it would not fall as the result of the transfer of mercury by the current. The tubes (B and C) of 5 mm. internal diameter joined the ends of the arc tube to capillaries DD of 0.5 mm. bore and 11 cm. long. Their purpose was to restrain oscillations but they were large enough to carry 5 amperes without undue heating. These were bent through 135°, and joined to parallel tubes, E,E, of 8 mm. bore and 20 cm. long, mounted on a grooved strip of wood. By supporting the lamp so that BAC sloped down and EF sloped upward, the latter could be boiled out in a few minutes through the capillaries and beyond by means of a Bunsen burner, no pump being needed. The open ends of the lamp led to short steel tubes FF soldered to leads GG of a 550-volt dynamo run by an induction motor. Arrangements were described also for operating the lamp under higher pressures obtained by means of a tire pump. At higher pressures this lamp was much more effective than arcs of greater section.

In a modified form the constriction was made only 38 mm. long, the ends of the tubes were open to the atmosphere and enlargements L,M, retarded changes in level due to the transfer of mercury. By putting the ends of a long U trough under the end of L and above M, the mercury transferred to the cathode trickled down the trough to the anode and made the operation automatic. Three amperes were required; for currents greater than 2 amperes, the constriction must be water-cooled.

In Table 9 the effect of variations of voltage and current upon the pressure in and the intensity emitted by such a constricted arc between 3650 and 3663 Å are listed. A 15-fold variation was made in the current and in the voltage, but not

Table 9.—Effect of Voltage and Current on Arcs.

Pressure, mm.	Volts per cm	Ampetes	Watts per mm ² × 10 ⁶
88	11.7	0.33	7.00
654	28.4	0.33	39.0
3920	57.6	0.33	268
29	7.4	1.00	15.0
208	13.8	1.00	43.0
664	21.4	1.00	137.
1398	28.2	1.00	392.
752	21.7	3.02	940
752	27.8	4.00	2090
752	29.5	5.00	2600

in these simultaneously; the result was a 160-fold variation in pressure and a 400-fold variation in the intensity of the 3660 line. The authors gave graphically the intensity vs. voltage-gradient curves at one ampere for six different wave-length maxima, as well as at 0.33 ampere (12.58 volts per cm.) for pressures ranging from 0.1 to 5 atmospheres. The first arc constructed had a section of 50 square

¹⁰⁹ Harrington, E. L. See also *Phil. Mag.*, (7) 4, 836 (1927).

¹¹⁰ Vincent, J. H., and Biggs, G. D., *J. Sci. Instruments*, 1, 242 (1924).

¹¹¹ Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, 11, 99 (1925); *J. Am. Chem. Soc.*, 47, 2449 (1925).

mm., a later one of about 3. The curves for the first showed a sharper bend and a straighter upper portion; those of the constricted arc showed a more uniform curvature. The curves for the larger arc bent and began to ascend steeply at about 6 volts per cm., but in those of the constricted arc this occurred at about 20 volts per cm. There was no evidence of a decrease in efficiency as the pressure increased up to five atmospheres.

The absorption of all lines, especially of 2537A, the shortest mercury arc line of sufficient intensity for general use in photochemical work, was diminished in the constricted arc. This line could be kept at constant intensity by tripling the current from 0.33 to 1.00 ampere, and cutting the voltage down from 62 to 32 volts per cm., thereby reducing the pressure from 4000 to 1500 mm. The greatest advantage of this type of arc seemed to lie in its high internal resistance, giving higher efficiencies at normal pressures, so that an increase in current becomes more nearly equivalent to an increase in voltage in the production of higher intensities. There was a tremendous relative increase in the 3663A line at high currents, while all the ultraviolet maxima except that at 2537A showed higher relative values at high currents.

For studying reactions with very low photochemical yields, there is required a source giving very great light intensities with at the same time a high degree of spectral resolution. These requirements were most nearly met by a portable constricted arc between two mercury surfaces, confined in a water-cooled quartz tube of 2 mm. internal, and 7-mm. external, diameter, 38 mm. long, with its ends open to the atmosphere. This lamp could be repaired easily and could be refilled and boiled out in ten minutes. There were no sealed-in leads to fail, no possibility of damage on reversing the polarity, and no tungsten electrode to sputter, the latter being a chief cause of the decrease in ultraviolet output of other arcs.¹¹² The constricted arc furnished (per square millimeter of exit slit of a monochromator) energy flux up to 30 times that available from a commercial lamp run at normal rating.

A further modification was designed by Leighton and Forbes¹¹³ to combine as fully as possible the long life of large diameter arcs with the high intensity of the constricted arc. The legs of an inverted U of 6 mm. internal diameter dipped into mercury reservoirs left open to the atmosphere. A 5-mm. capillary, nearly filled with an iron wire, attached to each arm of the U rendered oscillation negligible. The electrodes were water-cooled, and by adjusting the relative heights of the water and electrode surfaces, mercury transfer was neutralized. The distribution of the energy flux (determined by the aid of a monochromator and thermopile) is given in Table 10.

Table 10—Distribution of Energy Flux.

A	10,140	5770	4350	4060	3660	3130	3020	2800
Ergs/sec. mm. ²	325	910	490	360	900	610	420	100
A	2700	2540						
Ergs/sec. mm. ²	150	99						

Crist¹¹⁴ gave directions for making an arc that will run at 4 to 4.5 amperes and 20-25 volts per centimeter for over thirty hours with fairly constant intensity.

¹¹² Fabry, C., and Buisson, H., *Compt. rend.*, **153**, 93 (1911).

¹¹³ Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **51**, 3550 (1929).

¹¹⁴ Crist, R. H., *J. Am. Chem. Soc.*, **52**, 4337 (1930).

He later ¹¹⁵ put a transverse magnetic field across the arc to displace the latter to the back wall, thereby decreasing devitrification at the front wall. Other capillary mercury-vapor lamps have been described by Heidt and Daniels,¹¹⁶ by Heidt and Forbes,¹¹⁷ and by Hoffman and Daniels.¹¹⁸ The model of Forbes and Heidt eliminated cemented joints and the objectionable capillaries used in the earlier lamps to check mercury oscillations. Quartz tubing of 8-mm. internal diameter was used. Figure 57 is an axonometric view of the device, which was about 30 cm. in height. One feature of the apparatus is the tapered "Pyrex" plungers P, ground into tapers in the quartz walls at J. After the lamp is filled, these plungers are lowered

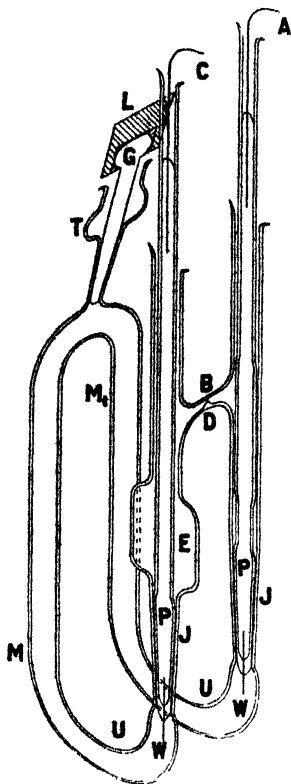


FIGURE 57.

Quartz Mercury-vapor Lamp of Forbes and Heidt (*Journal American Chemical Society*).

until oscillations of mercury are negligible, but the plungers are not lowered quite enough to close the joints completely; otherwise the lamp will melt or blow up. Tungsten wires W are sealed into the ends of the plungers, and when the latter are filled with mercury, a current path of negligible resistance, incapable of arcing, is provided. The two tubes U stand in open rectangular copper tanks (not shown), about 160 mm. (right) and 60 mm. (left) deep. Obviously, the length of either side of the arc (in one case, 150 mm. from M to M₁) can be changed by varying

¹¹⁵ Crist, R. H., *J. Am. Chem. Soc.*, **54**, 3939 (1932).

¹¹⁶ Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, **52**, 2151 (1930); **54**, 2381 (1932).

¹¹⁷ Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **53**, 4349 (1931).

¹¹⁸ Hoffman, R. M., and Daniels, F., *J. Am. Chem. Soc.*, **54**, 4226 (1932).

the depth of the corresponding tank. Tubes soldered in, top and bottom, permit rapid circulation of water.

The lamp is filled and boiled out through the tap T, provided with a ground-in quartz plug G held down by the lead weight L and sealed with mercury. The tap is bent 30° from the vertical, to prevent hot air ascending during operation from distilling the mercury out of the lamp. After closing the circuit through a suitable resistance, the arc is started by holding a flame below T. This arc sinks to the water surfaces, and operates at 3.5 amperes and 170 volts. As a much larger amount of mercury is displaced on the cathode side, the enlargement at E is necessary to accommodate it. As the mercury distills from the hot cathode to the cooler anode, it returns by the bridge B, which has a dam D to break up the trickles into

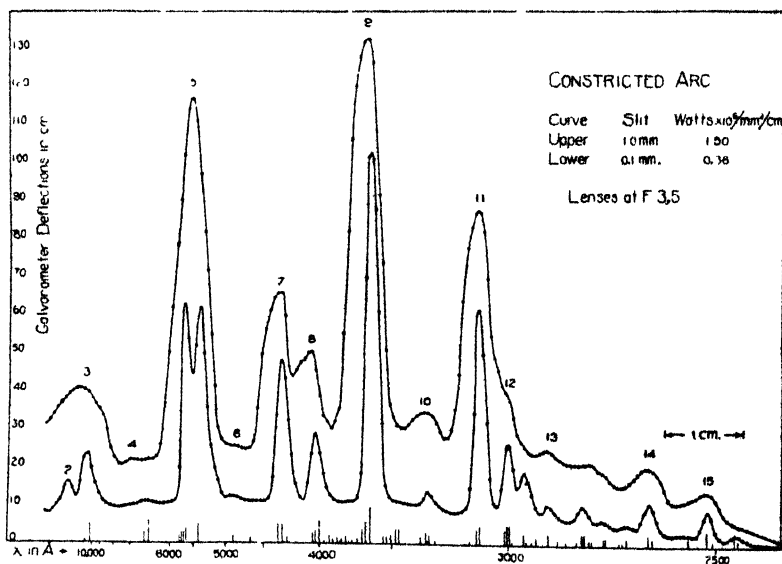


FIGURE 58. Spectral Energy Distribution Curves for the Constricted Arc (Forbes and Harrison, *Journal American Chemical Society*).

drops and thus avoids momentary short circuits. With a steady source of current, and nearly constant barometric pressure and ventilation, the total variation in light intensity over considerable periods seldom exceeds 3 per cent.¹¹⁹

Forbes and Harrison¹²⁰ presented a wave-length vs. energy curve (Figure 58) for a constricted arc in a water-cooled quartz tube of 2 mm. internal and 7 mm. external diameter, 38 mm. long with its ends open to the air and running on 3 amperes and 90 volts. A monochromator was used as a spectroradiometer. The lower curve, showing greater resolution, was obtained with an entrance slit of 0.1 mm., and the upper one with 1 mm. In the latter case, 140 ohms resistance was in series with the galvanometer and thermopile so that 1.0 cm. deflection corresponded to 1.50 microwatts per square millimeter at the exit slit. In the lower curve, 0.36 microwatt was the corresponding figure. Along the wave-length axis are short,

¹¹⁹ For a simple magnetic method of starting this lamp, see Wilson, L. D., *J. Am. Chem. Soc.*, **58**, 856 (1936).

¹²⁰ Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2449 (1925).

vertical lines indicating the number and approximate relative intensities (in a given group) of the various lines making up each maximum, as determined from a spectrogram of the light from the arc taken with an instrument of higher resolving power; the weaker lines are all relatively fainter than indicated. At the highest intensities used with the constricted arc, 490 microwatts per square millimeter of approximately monochromatic light of 3660Å were issuing from a monochromator slit 1×40 mm. or a total energy flux of about 196,000 ergs per second. Elenbaas¹²¹ has described a water-cooled constricted arc which operates under mercury pressures of 5 to 25 atmospheres.

In working with laboratory-made lamps, caution must be taken to avoid mercury poisoning. Attention was directed to the insidious onset of mercury poisoning and to the difficulty of cure by Stock,¹²² who described details of hygienic measures which should be taken in laboratories where work with mercury is conducted. Stock asserted that 0.01 or 0.001 mg. daily produces disturbances of the health. His warning excited considerable comment,¹²³ much, but by no means all of which, was confirmatory. The importance of the matter makes thorough toxicological studies highly desirable. Aside from the question of toxicity, there is a recorded instance of the explosion of a quartz mercury lamp, filling the laboratory with dangerous vapors and igniting nearby flammable materials.¹²⁴

A discussion of the impurities of mercury and the methods recommended for purification of the latter has been given by Booth and Jones,¹²⁵ who also describe in detail an unbreakable still capable of distilling three to five kg. of mercury per hour.

Water-Cooled Arcs. It is possible to lessen the absorption of the resonance radiation within the lamp by converting the latter into a low pressure arc by immersing the cathode in water. This procedure is not recommended in the case of commercial arcs. This caution does not, however, apply to those arcs, chiefly sold for therapeutic applications, which are designed for water-cooled operation. The arc is in this case operated with practically the same high voltage, high pressure and medium current density natural for air cooled arcs.

A design of a mercury-vapor lamp yielding nearly "cold light" is described by Billon-Daguerre, Medard and Fontaine.¹²⁶ The lamp is in the form of an inverted U-tube and is made of fused silica. Electrodes of Invar enter the ends of the tube. A short intense arc is formed at the bend of the tube between the columns of mercury on either side. The lamp is enclosed in a transparent silica flask (the wall of which is paraboloidal and silvered to act as a reflector) and is immersed in a tank of water. The light is concentrated by the mirror and emerges through a silica window in the tank. The lamp consumes 18 amperes, either alternating or direct current at 70 volts, and yields 3000 candlepower. The light can be used for microscopy and projection work without heating the specimens or celluloid films. The mercury lamp is said to possess an advantage over the carbon arc in that the

¹²¹ Elenbaas, W., *Rev. optique*, 15, 343 (1936). See also Harada, T., and Azuma, T., *Proc. Phys.-Math. Soc. Japan*, 19, 677 (1937); *Chem. Abs.*, 31, 8365 (1937); Egyesült Izzólampa és Villamosági Rt., British P. 482,070, March 23, 1938; *Chem. Abs.*, 32, 6562 (1938), Bol. C., *Phys. Rev.*, 52, 214 (1937).

¹²² Stock, A., *Z. angew. Chem.*, 39, 461, 984 (1926); 41, 663 (1928); *Biochem. Z.*, 216, 243 (1929).

¹²³ Schmidy, A., *Z. angew. Chem.*, 39, 786 (1926); Pincus, G., *Ibid.*, 787; Reihlan, H., *Ibid.*, 788; Wolf, L., *Ibid.*, 789; Ruska, J., *Ibid.*, 790 (1926); Hoffmann, F. G., *Chem. Ztg.*, 50, 927 (1926); Holtzmann, Z., *angew. Chem.*, 40, 438 (1927); Winderlich, R., *Chem. Ztg.*, 52, 629 (1928); Kröner, W., *Chem. Ztg.*, 52, 121 (1928); Podrouzek, R. N. V., *Chem. Listy*, 22, 529 (1929).

¹²⁴ Mechlin, F. J., *Ind. Eng. Chem.*, 19, 859 (1927).

¹²⁵ Booth, H. S., and Jones, N. C., *Ind. Eng. Chem.*, 19, 104 (1927).

¹²⁶ Billon-Daguerre, A. L., Medard, L., and Fontaine, H., *Compt. rend.*, 157, 921 (1914).

luminous point remains fixed and requires no regulation. Application of such lamps to water sterilization and submarine photography has been suggested.

Bates and Taylor¹²⁷ developed a cooled arc of C702P "Pyrex" glass with tungsten leads. Through the center were two concentric quartz tubes, R_1 and R_2 (Figure 59). R_1 is the reaction vessel for photochemical changes while R_2 is a water-jacket to prevent R_1 from becoming overheated by the action of the arcs. Outside, the glass system was sealed to quartz by rubber tape and by Gooch crucible tubing, wired and shellacked to permit operation of the arc at 100°C. The seals were protected by coils of lead pipe D carrying cold water. N is the negative electrode and A, B, C_1 and C_2 are all positive. N and A are tungsten leads covered by just enough mercury to cause the two surfaces to come together on jarring. An arc is formed which jumps to B, a nickel cone welded to tungsten.

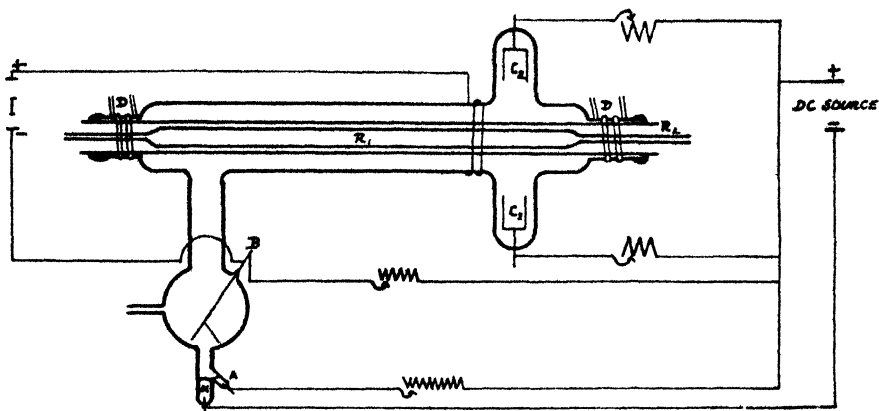


FIGURE 59. Mercury Arc for Study of Mercury-Sensitized Photochemical Reactions (Bates and Taylor, *Journal American Chemical Society*).

This serves as an electrode and also deflects mercury vapor from N against the walls of the bulb, kept in a water bath. This regulates the vapor pressure in the arc to that of mercury at the bath temperature. The arc can be brought up to the electrodes C_1 and C_2 by breaking down the space charge by an induction coil, the secondary of which is shown at I. C_1 and C_2 are two cylindrical nickel electrodes. The potential necessary depends to a large extent on the geometry of the arc. R_2 is 2.5 cm. in diameter and 45 cm. long, R_1 1.5 cm. by 37 cm., the surrounding glass arc being 40 cm. by 5 cm. The side tubes containing C_1 and C_2 are 3.5 cm. in diameter and 5 cm. long. The side tube with bulb and mercury reservoir is 30 cm. long and 3.5 cm. in diameter, while the diameter of the bulb is 6 cm. This has a drop of 35 volts from C_1 and C_2 to N when running at 18 amperes. The slide-wire resistances are of such size and capacity that the current from A to N is 0.5 ampere, B to N, 5 amperes, and from C_1 to C_2 to N up to 10 amperes each. C_1 and C_2 must have separate resistances or the current would flow entirely to one of them, giving an unevenly distributed discharge. After the arc has been started, B may be disconnected, but A should remain in the circuit to insure a steady arc. Due to leaks around the seals, the arc can be run only with a mercury pump in con-

¹²⁷ Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, 49, 2438 (1927).

tinual operation. If the arc is run with air in too large quantity, not only do the electrodes become oxidized, causing the arc to emit a pink glow, but the mercury tends to wet the glass between A and N making it impossible to start the arc. When the arc is first set up or after a long period of disuse, the nickel electrodes must be degassed by the passage of a current greater than that ordinarily used. The temperature of the water in R₂ should be kept above that of the bulb to prevent distillation of mercury from N, which would cut down the light.

A water-cooled lamp of the mercury anode type is in extensive use for medical work. The cooling serves to protect the tissues from the heat of the arc, so that it is possible to secure a high intensity of ultraviolet, particularly in the short-wave region, by reducing the distance between the source and the area treated. The lamp has a U-shaped quartz tube, A, the bend of which is in a plane perpendicular to the plane of the arms. (Figure 60.) The tube carries on the ends two mer

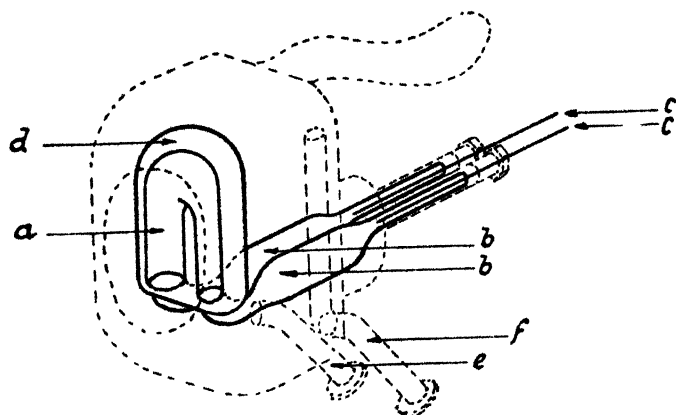


FIGURE 60. Kromayer Lamp.

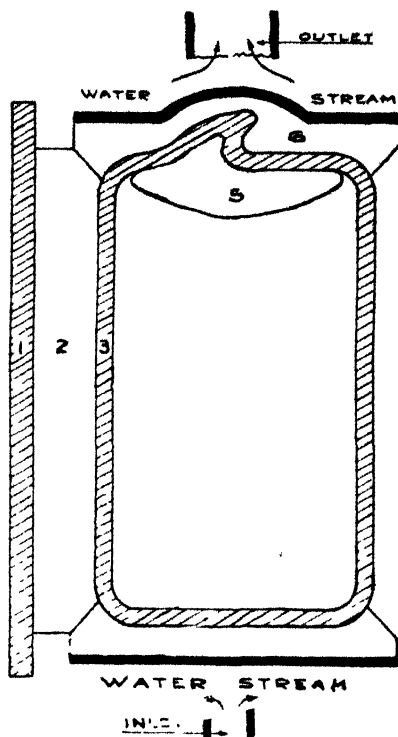
cury containers *BB* at right angles to the plane of the arc tube, and these constitute the electrode vessels to which the current is conducted by ground-in mercury-sealed rods *CC*. The arc is formed in the portion of the tube which is surrounded by a jacket of quartz, so shaped as to maintain an approximately equal distance between the walls of the tube and the envelope, to make the cooling uniform. The space is filled with a suitable gas, the thermal conductivity of which affects the electrical characteristics of the arc.¹²⁸ Between this jacket and the outer housing of the apparatus, water is circulated. The light is emitted through a quartz window in front of the casing, after passing through a layer of water. The compact form made possible by this construction, known as the Kromayer,¹²⁹ is advantageous for many purposes. A form with a double anode for alternating current operation also has been prepared.

Other manufacturers, notably the Burdick Corporation, employ the Uviarc as the source for a water-cooled lamp. The infrared rays are removed by a sealed quartz filter cell containing pure water. The cell is incompletely filled to permit

¹²⁸ Anderson, W. T., Jr., U. S. P. 1,749,994, March 11, 1930 (to Hanovia Co.); British P. 296,527, Sept. 6, 1928; French P. 638,802, Aug. 3, 1927; British P. 356,056, Sept. 3, 1931.

¹²⁹ Hanovia Chemical and Manufacturing Co.

expansion of the water as the lamp heats up. A stream of flowing water surrounds the filter cell and serves to cool it. This stream of water does not come into contact with any quartz surface through which the rays must pass, eliminating any loss of transparency due to the deposition of solids. An air-space between the filter-cell and the quartz face of the lamp further eliminates heat by conduction. See Figure 61. An automatic shutoff to protect the lamp when the water flow fails has been described by Piatti.¹⁸⁰ Another liquid-cooled lamp for photochemical work is due to Goltstein.¹⁸¹



Courtesy Burdick Corporation.

FIGURE 61.

Ever-Clear Window of Burdick Water-cooled Lamp. Cross Section: Side View. 1. Quartz outer face. 2. Air space to eliminate heat by conduction. 3. Fused quartz window. 4. Lens of distilled water to filter out infrared. 5. Evacuated space to allow for expansion of water. 6. Soft-metal case to protect the quartz window.

THE DETERIORATION OF QUARTZ MERCURY ARCS

Deterioration of the lamps was a serious problem to the earlier manufacturers of mercury arcs. The literature is filled with many observations of lamp failure. Poorly constructed lamps caused some of these.¹⁸² Others were inaccurate because of the use of unsatisfactory actinometric methods for measuring the output.

In early lamps, Coblenz found that the percentage of the total radiation shorter than 4500Å decreases from an initial value of 70 per cent to about 50 per cent after 1000 to 5000 hours. This included the strong groups of lines at 4360 and 4060Å.

¹⁸⁰ Piatti, L., *Physik. Z.*, 31, 182 (1930).

¹⁸¹ Goltstein, E., U. S. P. 1,669,819, May 15, 1928; *Chem. Abs.*, 22, 2296 (1928). For a recent inexpensive source of mercury resonance radiation of high intensity, see Steacie, E. W. R., and Phillips, N. W. F., *Can. J. Research*, 16B, 220 (1938).

¹⁸² See, e.g., Bordier, H., *Arch. Elec. Med.*, 1910, 396; Courmont, J., and Nogier, T., *Compt. rend.*, 152, 1746 (1911); *Illuminating Engineer*, London, 4, 503 (1911); Le Bon, G., *Compt. rend.*, 153, 49 (1911); Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, 44, 453 (1925).

The total output decreased to about one-half to one-third of its initial value.¹⁸⁸ Thermopile observations showed no marked difference in the proportion of ultraviolet emitted during the first 500 hours of use. The data of Table 11 represent the output as measured in galvanometer scale deflections.

Table 11.—Effect of Age upon Radiation.

Age in hours	0	97	177	343	450	522	640	783	959	1064	1140
Total radiation below 14,000A	1611	1497	1503	1380	1033	910	1104	1107	1069	1025	1034
Ultraviolet less than 4500A as % of total	69.4	67.8	60.4	...	59.9	58.2	54.8	52.3	50.8	...	49.1

Nelson¹⁸⁴ found that a burner (Curve A, Figure 62) which had been used for 500 hours had lost none of its effectiveness in testing ageing on paints. Another burner, B, was first used for 1600 hours, at which time its effectiveness had decreased markedly. The deposit on the surface of the quartz was then removed

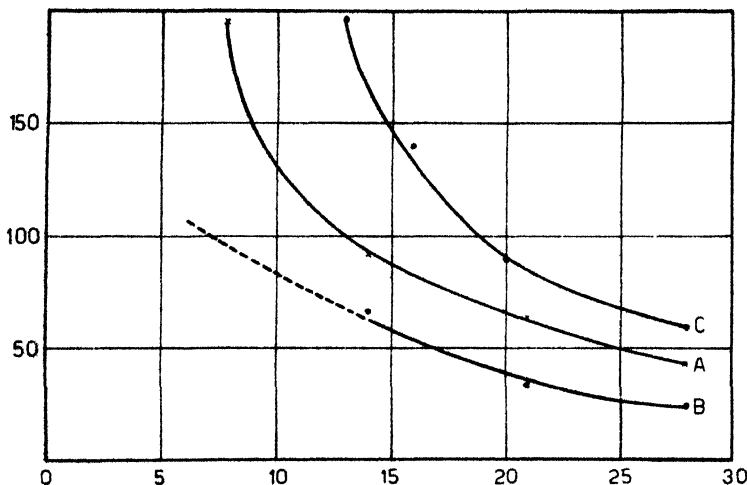


FIGURE 62. (Nelson, *Proceedings American Society for Testing Materials*.)

as far as possible by heating the quartz with a blast burner and the lamp again used for 250 hours. The relative intensities of the two burners A and B in the region shorter than 3100A were found to be in the ratio of 1.7 to 1 when used at 220-240 volts and 6.5 amperes, indicating a decrease of about 40 per cent for the old burner.

Reeve¹⁸⁵ found by physical methods that 500 hours of use caused a decline in the intensity of a commercial lamp at 2540A of 60 per cent and of the 3660A lines of 28 per cent. Thus, the decrease is most marked in the extreme ultraviolet. It

¹⁸⁸ Coblentz, W. W., Long, M., and Kahler, H., *J. Frank. Inst.*, **187**, 112 (1919); *Bureau of Standards Sci. Papers*, 330 (1918). Note also *Sci. Papers* 378 and 495.

¹⁸⁴ Nelson, H. A., *Proc. Am. Soc. Testing Materials*, **22**, II, 485 (1923).

¹⁸⁵ Reeve, L., *J. Phys. Chem.*, **29**, 39 (1925); Cunliffe, P. W., Franklin, R., Maddison, R., and Reeve, L., *Ibid.*, **30**, 1427 (1926).

was believed that for arcs employed in quantitative work in the region 2480 to 2890A, the energy distribution should be determined every 200 hours. The energy in this region was thought to be considerably reduced during the first 500 hours. The 2485A line sometimes disappeared within 100 hours and the 2300, 2340, 2370 and 2400A lines were ineffective after less than 50 hours. Similar observations were recorded by Gillam and Morton,¹³⁶ who believed that after a rapid fall in the output of the extreme ultraviolet in the first 150 to 200 hours, the output becomes fairly constant. After this first change, there occurs a slow nonselective loss in transmission of the burner. The first effect was thought due to the formation of SiO vapor inside the lamp and the second to the gradual deposition of a film of opaque silicon.

Hanovia lamps (Luxor B Alpine Sunlamp) are said to drop to 80 per cent of their initial emission in the first 300 hours, after which they remain fairly constant showing 73 per cent after 2000 hours.

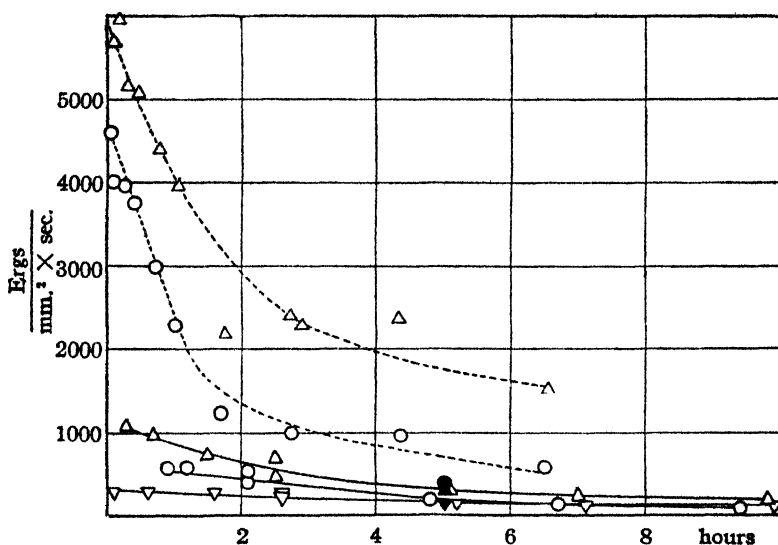


FIGURE 63. Rate of Deterioration of Constricted Lamp (Forbes and Harrison, *Journal American Chemical Society*).

Flynn¹³⁷ suggested that for a 220-volt lamp, an increase in the voltage at the rate of two volts per 100 hours of operation would compensate for the ageing loss.

Kolbert¹³⁸ proposed a circuit with variable resistance coil or tapped transformer and control switch marked on the dial so as to operate a lamp at 140, 150, 155, 160, 165 and 170 volts after 100, 250, 400, 600, 800 and 1000 hours, respectively. The manufacturers of the Uviarc recommended that during the first 500 hours the voltage be increased 3 per cent each 100 hours.

Devitrification in quartz plays only a secondary role in ageing, according to Meyn.¹³⁹ There is a black deposit on the inner surface, a part of which can be

¹³⁶ Gillam, A. E., and Morton, R. A., *Phil. Mag.*, 6, 1123 (1928).

¹³⁷ Flynn, O. R., *Am. Dyestuff Repr.*, 12, 837 (1923).

¹³⁸ Kolbert, J. W., *British P.* 413,921, July 26, 1934, to British Hanovia Co., Ltd.

¹³⁹ Meyn, W., *Z. wiss. Phot.*, 23, 345 (1927); *Brit. Chem. Abs.*, 677, B (1928).

rubbed off or removed by acids. Another deposit penetrated to a depth of 0.1 mm. and was thought to be either finely-divided mercury or elemental silicon. Buttolph has published a photomicrograph taken by Dr. Hodge of the Stevens Institute ¹⁴⁰ of the inner surface of a glass tube of a mercury arc. The surface was densely and uniformly pitted. This probably occurs also in quartz tubes, increases with increased temperature, voltage or any other factor that increases bombardment by electrons or by mercury molecules or ions. In burners with tungsten anodes, sputtering of these has long been recognized as a factor in ageing. Figure 63 shows the rate of decline in energy per sq. mm. of exit slit of the constricted arc for three wave-lengths.¹⁴¹ Inverted triangles indicate 4060A, upright triangles 3660 and circles 2540A. Dotted lines give the output of the constricted arc on 94 volts and 4.9 amperes, solid lines on 78 volts and 2.1 amperes. All intensities were multiplied by ten. The three blacked-in points indicate a new commercial arc on 82 volts and 4.1 amperes. A new constriction was inserted before the run with 2.1 amperes and this was cleaned and revitrified before that with 4.9 amperes. The deterioration of the constricted arc is rapid, being 50 per cent for the first hour at 2540A and 5 amperes. This rate falls off greatly with increase in time and wave-length and with decrease in current.

¹⁴⁰ Buttolph, L. J., *Trans. Electrochem. Soc.*, **65**, 148 (1934).

¹⁴¹ Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2453 (1925).

Chapter 8

Mercury Discharge Lamps

Since the radiations from a mercury lamp are emitted from mercury vapor in the positive column, it is evident that, if mercury vapor is made to fill the lamp by vaporization from any reservoir, a mercury cathode is not essential. George¹ devised a lamp in which tungsten electrodes were used and the mercury was vaporized from a separate spherical bulb connected with the quartz tube by a narrow-bore tube. Before the lamp had heated up sufficiently to vaporize the mercury, the discharge was carried by an inert gas under pressure. George² stated that the ultraviolet output might be increased by using alternating current at high voltage and frequency. The terminals were connected with the inductance of an oscillating circuit, although other ways of converting local alternating current to a high frequency were also suggested.

The use of tungsten cathodes as a source for the emission of electrons at high voltages was limited by their tendency to sputter and blacken the lamp envelope. Greater progress was based upon the discovery by Wehnelt³ that calcium oxide fused onto the surface of heated platinum forms a cathode of high electron emissivity at lower temperatures than are necessary for tungsten. Such cathodes were employed in the construction of lamps by Konen and Jungjohann.⁴ According to Buttolph,⁵ in more recent developments, nickel has replaced platinum as the base. Much work has also been done upon the development of cathodes in which alkaline-earth oxides with various additions have been applied to spirals of wire.⁶ The theory of the operation of this type of cathode, and particularly, of the manner in which the physical or chemical union of the coating and base material affects satisfactory operation, lies beyond the scope of this book.⁷

The oxide-coated type of cathode can also be made with such elements as sodium and caesium.⁸ The choice of metal and activating coating depends on the operating temperature, vapor pressure and other features of the design. In some cases, the oxide-coated cathodes are brought to the necessary cathode temperature directly by the cathode voltage drop and arc current. This is the arrangement in the low-voltage Cooper-Hewitt mercury rectifier lamp and in the high intensity mercury arc of the General Electric Vapor Lamp Co. In some cases, they receive a preliminary heating by a glow discharge facilitated by a starting gas. Because of the rather

¹ George H., U. S. P. 1,361,710 (1920); *J. Soc. Chem. Ind.*, 40, 75A (1921).

² George, H., U. S. P. 1,671,109, May 29, 1928; British P. 234,834, March 18, 1926.

³ Wehnelt, A., *Ann. Physik*, 14, 425 (1904).

⁴ Konen, H., and Jungjohann, W., *Verhandl. deutsch. Physik. Ges.*, 3, 145 (1910).

⁵ Buttolph, L. J., *Trans. Illum. Eng. Soc.*, 28, 153 (1933); 30, 151 (1935).

⁶ Spanner, H. J., and Doering, U. W., British P. 397,162, Aug. 8, 1933; Meyer, F., and Spanner, H. J., British P. 274,027, Oct. 20, 1927; Germer, E., French P. 707,198, April 13, 1931; Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Spanner, H. J., Doering, U. W., and Germer, E., German P. 597,580, May 26, 1934.

⁷ Dushman, S., *Rev. Modern Physics*, 2, 381 (1930); Reimann, A. L., *Phil. Mag.*, 12, 1073 (1931); Becker, J. A., *Phys. Rev.*, 34, 1323 (1929); Druyvesteyn, M. J., and Warmoltz, N., *Physica*, 4, 41 (1937); Suhrmann, R., and Frühling, G., *Naturwiss.*, 26, 108 (1938).

⁸ Becker, J. A., and Sears, W., *Phys. Rev.*, 38, 2193 (1931); Benjamin, M., and Rooksby, H. P., *Phil. Mag.*, 15, 810 (1933).

limited heat available for starting and for operation, the lamps are made as small and of as low a heat radiating and heat capacity as possible. In other lamps, the cathodes are separately heated by special elements. A number of cathodes have been described by Buttolph.⁹

The gas or metal vapor conducting arcs may be designed for the utilization of the emission of the radiations from the positive column, as in tubular lamps, or of that of the negative glow as in certain lamps of bulbular form. It is not possible to give an account of the many varieties of these lamps which have been proposed. Since much of the development of these lamps as ultraviolet sources has been intimately associated with the development of lamps for visible lighting, an historical account would involve much extraneous material. It is interesting to note that the development of modern gaseous conduction lamps has been based in large part upon the pioneering work of McFarlan Moore.¹⁰

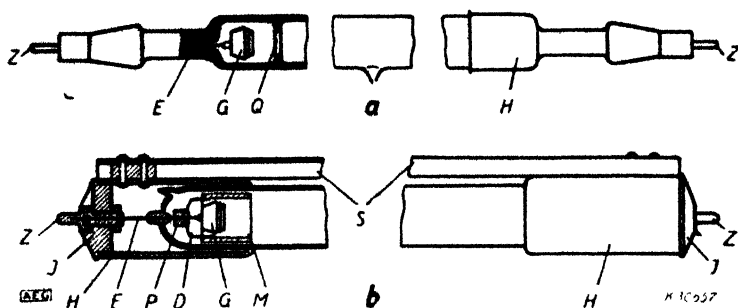


FIGURE 64. *a*, S, Burner of Quartz; *b*, S, Burner of I-G Phosphate Glass (Ende, *Z. technische Physik*.)

When the amount of mercury is such that no liquid or solid metal is present during operation of a lamp the static characteristic of the latter is not based upon the principles outlined in the previous chapters. Such lamps¹¹ are less affected by the temperature of the surroundings. As the load increases, the current increases markedly, but in contrast to the lamps described in Chapter 6 increase in voltage does not affect the operation of the lamp. The current can be adjusted by the series resistance rather than by ventilation, and the necessity for cooling is eliminated. The absence of the liquid mercury phase increases the stability of the lamp and also permits operation of the latter in any position. Bruijnes¹² pointed out that an excess of mercury might diminish the efficiency of a discharge tube by condensing on the walls and absorbing the ultraviolet. He described a discharge tube within which there was inserted a quartz tube. The latter was utilized to hold the material to be subjected to ultraviolet irradiation.

The lamp described by the Hanau Quarzlampen A.-G. uses special nickel-oxide-coated electrodes of basin-like members piled one on another. Argon at a few mm. pressure in the lamp serves to supply ions for conduction until the mercury, introduced as a small button of some hundredths of a gram sufficient to produce a vapor

⁹ Buttolph, L. J., *Trans. Illum. Eng. Soc.*, **28**, 153 (1933); **30**, 151 (1935). See also Hull, A. W., *Trans. Am. Inst. Elec. Eng.*, **47**, 753 (1928); Found, C. G., and Forney, J. D., *Ibid.*, 747.

¹⁰ Moore, McFarlan, *Gen. Electric Review*, **23**, 577 (1920).

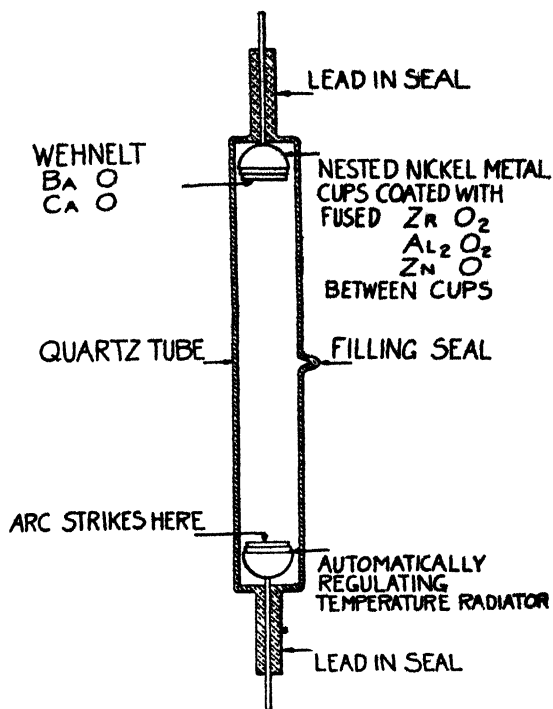
¹¹ British P. 399,317, October 5, 1933, to Quarzlampen-Gesellschaft m.b.H., Hanau.

¹² Bruijnes, J., U. S. P. 1,994,301, March 12, 1935, to General Electric Co.

pressure of 700 mm. (corresponding to $350^{\circ}\text{C}.$), carries the discharge. Ignition is facilitated by the presence of a strip of Aquadag on the outside wall connected with the electrodes and interrupted in the neighborhood of one of them. This serves as a grounding device which collects electrostatic charges from the walls.¹³ Very similar principles are employed in the therapy lamp (Alpina Heimsonne)¹⁴ developed by that company. The therapy lamp is 10 to 20 cm. long and is enclosed in a special phosphate glass rather than in quartz. The glasses employed soften at $560^{\circ}\text{C}.$ and, therefore, cannot stand the weight of masses of mercury but can be used with the self-igniting solid oxide electrodes which heat during the discharge. A millimeter of this glass transmits 34 per cent of the radiation of wave-length 2500A. When cool, the mercury condenses on the inner walls of the tube, the

FIGURE 65.

Quartz Burner Showing the Electrode Arrangement (Anderson and Bird, *Journal Optical Society of America*).

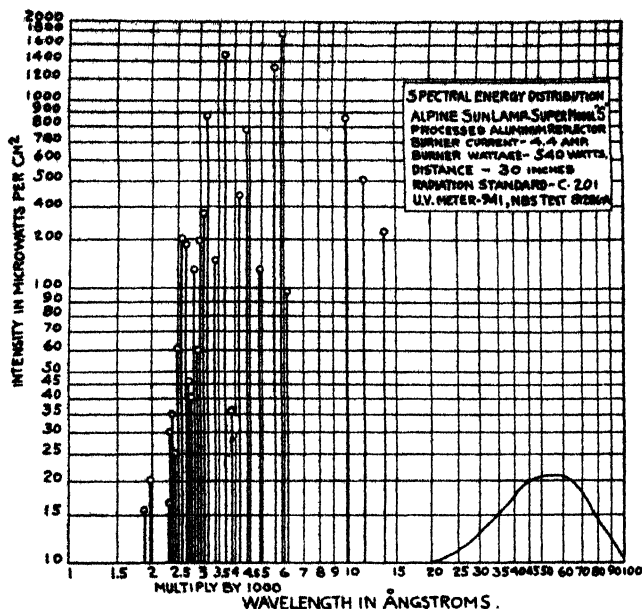


dimensions of which are so chosen that the discharge space is brought to $350^{\circ}\text{C}.$ at its coolest spot, but nowhere exceeds $560^{\circ}\text{C}.$ To secure this temperature, special pole-caps and metal protective mantles were placed about the electrodes to prevent the temperature of the glass in this region from approaching the softening point. The lamp is ballasted at 1.8 amperes, 120 volts burner tension for the 17 cm. arc, and worked at a point on the burner characteristic which, at 220 volts and 62 ohms, is still so far from the labile point that the discharge does not extinguish if the tension drops by 20 volts.

Figure 64 shows a section of the lamp. A glow electrode (G) sits on the sealed-in wire (E). The protective coat (M) is borne by two wires (D) joined

¹³ See Spanner, H. J., U. S. P. 1,860,210, May 24, 1932.

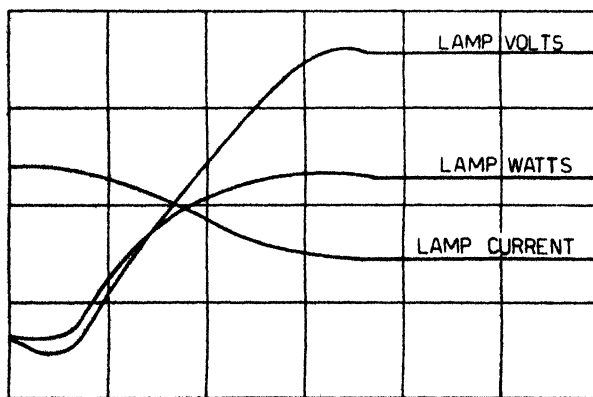
¹⁴ Ende, W., *Z. tech. Physik*, 15, 313 (1934).



Courtesy Hanovia Chemical and Manufacturing Co

FIGURE 66. Spectral Energy Distribution of Alpine Sun Lamp, Super Model "S."

to E, but insulated from E by glass (P) to prevent arcing to the mantle. The electrode is buried 10 millimeters within the mantle for better heat protection. The pole vessels are externally covered by a metal sheath (H), closed off by an insulating cover plate (I), through which the current is admitted, (Z). The two end sheaths



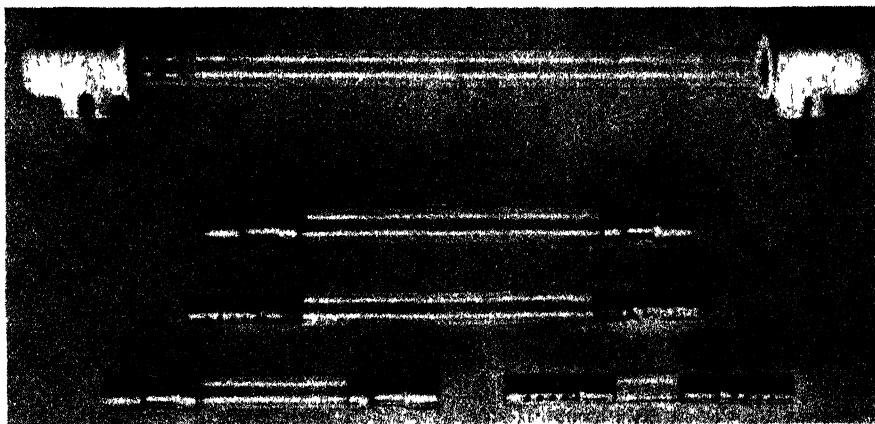
Courtesy General Electric Vapor Lamp Co.

FIGURE 67. Typical Starting Characteristics of 360-watt Uviarc.

are held by a long end-to-end shield which carries the whole burner. A transformer and accessory resistance are required. During starting, the voltage increases in proportion to the pressure for about six minutes, but there is a preliminary saddle

due to irregularities in heating up various parts of the tube before the arc burns steadily, after which the characteristic follows the usual hyperbolic curve.

Anderson¹⁵ uses a laminated electrode structure comprising pieces of metal separated by barium and calcium oxides. This principle is employed in the more recent models of the quartz lamp of the Hanovia Co. (Figure 65). The heat is radiated directly from the electrodes, which consist of a number of nested metal cups connected electrically and mechanically by a weld, and separated by the oxide coatings which automatically regulate the temperature. The 200-watt burner operates on 220 volts a.c., has a diameter of 16 mm. and an arc length of 130 mm. A ballast resistance or reactance must be used in series to limit the current. The life of the lamp is about 2000 hours. The spectral energy distribution of an Alpine Sun Lamp (Super Model S) at a distance of 30 inches is given in Figure 66. There was a processed aluminum reflector. The burner current was 4.4 amperes and its wattage was 540.¹⁶



Courtesy General Electric Vapor Lamp Co.

FIGURE 68. New Mercury Uviarcs.

Lamps of the newer type, which start automatically, reach stable operating conditions within about three minutes after starting. Figure 67 shows the typical starting characteristic of the 360 watt Uviarc.¹⁷ The new lamps of the General Electric Vapor Lamp Co. operate in conjunction with a high reactance type transformer. The reactance limits the discharge current, stabilizes the arc and minimizes the flicker in the radiation output. The transformer may also supply a leading current at relatively high voltage from an extension of the primary winding to a power factor correcting capacitor.

The lamps are supplied in five sizes (Figure 68) consuming 150, 250, 360, 600

¹⁵ Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Anderson, W. T., Jr., U. S. P. 1,902,936, March 28, 1933; Anderson, W. T., Jr., and Bird, L. F., U. S. P. 2,006,081, June 25, 1935; *J. Opt. Soc. Am.*, **27**, 95 (1937). Note also Siemens and Halske, A.-G., British P. 475,763, Nov. 25, 1937; *Chem. Abs.*, **32**, 3279 (1938); Elenbaas, W., U. S. P. 2,116,741, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

¹⁶ Personal communication, Hanovia Chemical and Manufacturing Co. See also Melville, H. W., *Trans. Faraday Soc.*, **32**, 1525 (1936).

¹⁷ Unpublished data of Johnson, L. B., and Webster, S. B., communicated by the General Electric Vapor Lamp Co. See also Inman, G. E., and Lemmers, E., U. S. P. 2,085,530 and 2,085,531, June 21, 1937; *Chem. Abs.*, **31**, 5698 (1937).

and 1200 watts. The radiation outputs of these burners at various wave-lengths in microwatts per sq. cm. at one meter are given in Table 12.¹⁸

Table 12.—Radiation Output of Mercury Discharge Lamps.

Wave-length (Angströms)	Burner Watts—				
	150	250	360	600	1200
	Microwatts per sq. cm. at 1 meter				
5780	37.3	60.2	83	255	510
5461	33.5	56.0	82	222	445
4358	28.5	45.5	72	192	385
4047	16.9	26.8	45	111	223
3654	49.6	78.5	122	327	654
3341	5.3	7.4	11.6	35	71
3129	32.6	50.8	85	203	406
3022	16.6	25.3	39.4	107	214
2967	8.8	13.5	20.9	56	113
2894	3.5	5.3	8.3	23	47
2804	7.0	10.9	15.7	42	85
2753	2.5	3.8	5.5	17	33.6
2700	3.0	4.4	7.6	20	40.2
2652	14.4	22.5	83.1	88	176
2537	15.5	27.8	47.4	103	207
2483	6.1	9.9	13.3	39	79.5

The 360-watt lamp with its transformer and reflector is shown in Figure 69. The 600- and 1200-watt tubes are intended primarily for industrial application where large, high-intensity sources are required.

The principle of the use of a discharge in mercury vapor at a low pressure in a noble gas frequently has been employed in sources intended for production of the resonance lines of mercury in physical laboratories. Pressure broadening of the mercury lines has been avoided by keeping the partial pressure of the mercury low. Kunze¹⁹ warmed mercury to 40°C. in a glow discharge in neon, employing a capillary tube to secure great surface brilliancy, although this opened the possibility of broadening by the intermolecular fields of ions in high current density. Houtermans²⁰ secured high currents and great total brilliancy by the use of a discharge tube with oxide cathodes, employing argon at 3-4 millimeters. This form of discharge (studied by Pirani²¹) is characterized by high strength and line sharpness. The discharge was started by a small induction coil or a medical high-frequency apparatus, it being necessary only to bring the high-tension electrodes near the lamp. The temperature of the mercury reservoir was regulated by placing the reservoir in a side-tube dipped in water. One part of the illuminating tube was compressed into a flat rectangle 30 millimeters square and 2 millimeters thick to maintain the discharge against the quartz wall and so lessen the effects of self-absorption. The width of the discharge depended upon the current, increasing with the latter at constant current density, but never completely covering the area of the rectangle. When the lamp was started, there was at first a self-maintained discharge, showing a Faraday dark space. In this state, the voltage drop over the lamp was high (180-200 volts) and the current but a few milliamperes, the lamp remaining cold. At a certain current value, the oxide cathode began to emit strongly, the voltage dropped to between 20 and 30 volts and the current rose. The current was not

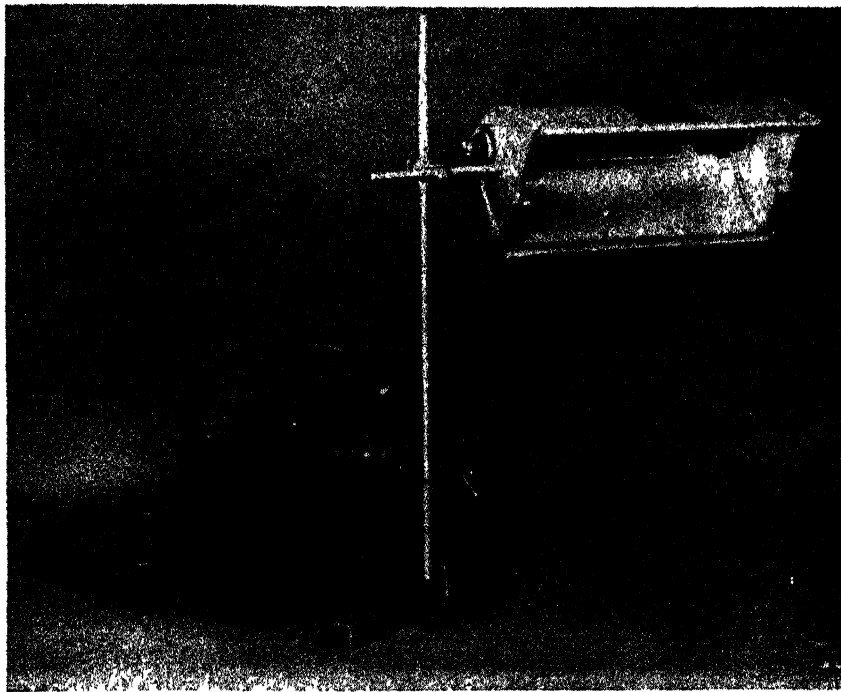
¹⁸ Communication from the General Electric Vapor Lamp Co.

¹⁹ Kunze, P., *Ann. Physik*, **5**, 793 (1930).

²⁰ Houtermans, F. G., *Z. Physik*, **76**, 474 (1932).

²¹ Pirani, M., *Elektrotech. Z.*, **51**, 889 (1930).

permitted to rise above 3.6 amperes to prevent the oxide cathodes giving off a dust which blackens the tube. During starting, however, the resistance could be momentarily removed, permitting a current of 4 to 4.5 amperes. At 24 volts and 2.6 amperes, the intensity could be kept constant within 2 per cent for over two hours. Such lamps could be used for some hundreds of hours without deterioration.



Courtesy General Electric Vapor Lamp Co.

FIGURE 69. 360-watt Uviarc for General Laboratory Use.

Kornfeld and Müller-Skjold²² devised a lamp which emits the line 2537A twelve times as intensely as does the usual mercury arc. The lamp operates at 220 volts and has water-cooled tungsten electrodes. The cathode is coated with a mixture of barium and strontium carbonates and is heated with current from a step-down transformer.

The Hanovia Co. now supply tubes in which 85 per cent of the emitted light is at 2537A. They are built to consume 30-100 milliamperes at 2000 or more volts. With an input of 25 watts, they supply 40 microwatts of 2537A radiation per square centimeter at 20 inches. They are available in various forms, straight, U-shaped and S-shaped, and usually have a tube length of from one to six feet. A form intended as a source for work on the Raman effect is shown in Figure 70.²³

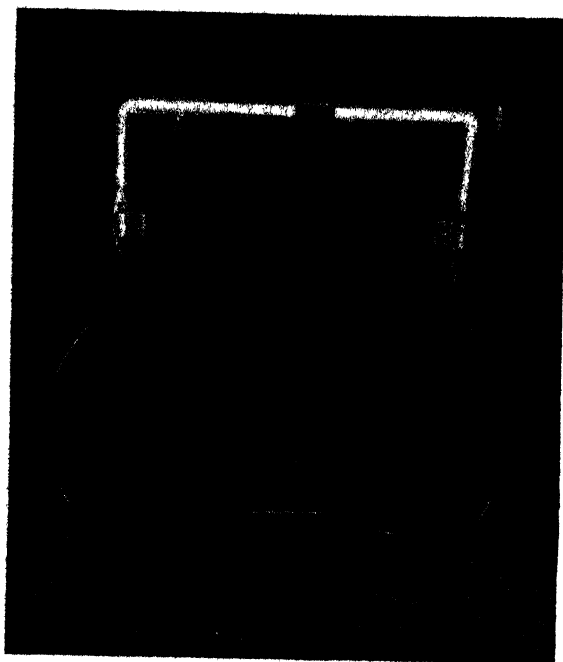
In one of the first lamps of this type, Wiegand²⁴ employed a discharge in

²² Kornfeld, G., and Muller-Skjold, F. *Z. physik. Chem.*, B31, 223 (1936).

²³ See Leighton, P. A., and Leighton, W. G., *J. Chem. Ed.*, 12, 139 (1935).

²⁴ Wiegand, K., German P. 509,373, Nov. 4, 1926; U. S. P. 1,971,887, August 28, 1934, to Patent-Treuhand-Ges. für Elek. G m b H.; *Chem. Abs.*, 28, 6371 (1934).

nitrogen or carbon dioxide and some hydrogen at low pressures in a quartz or Uviol bulb containing a drop of mercury. The mercury extended the radiations from the limit of the nitrogen radiations (2800A) to about 2200A and improved the distribution of the spectral lines. The tube carried only 50 to 80 milliamperes, and operated at a temperature so low that it could be operated in direct contact with the material to be irradiated. Other forms, differing in structural features, have been described by Foulke,²⁵ who uses the negative glow between two closely spaced (0.5-2.0 mm.) oxide-coated nickel electrodes, in a gas containing neon (75 per cent) and helium (25 per cent) and a small quantity of argon at 30 mm. pressure. A small quantity of mercury is also present. The metastable potential of the



(Courtesy Hanovia Chemical and Manufacturing Co.)

FIGURE 70. Hanovia Sc-2537 Tube for Raman Work.

major component is to be greater than the ionizing potential of the minor component. This lamp, contained in a fused silica or Pyrex container fitted with a base plug, is operated on 100-110 volts direct current or 75 volts alternating current. As a "getter" it contains a bead of alkali-metal oxide, hydroxide or carbonate. The lamp may be used for therapy, photochemistry, or ultraviolet signaling.

The G-1 or Glow Lamp of the General Electric Co. consists of two oxide-coated tubular filaments heated from within by tungsten filaments, a connecting and supporting bridge and center support to hold them, and a pool of mercury. It produces ultraviolet radiation by virtue of a glow discharge in the mercury vapor at low pressure throughout the entire bulb. Consuming approximately 40 watts, the lamp

²⁵ Foulke, T. E., British P. 361,394, July 21, 1931, to the British Thomson-Houston Co., Ltd.; U. S. P. 1,990,174-5, February 5, 1935, to General Electric Vapor Lamp Co.

starts at a current of two amperes at 35 volts, and operates at 20 volts and two amperes. A separate small transformer is required for each lamp. It emits but little visible light.²⁶

A number of lamps have been patented by the Philips Lamp Works. In one form²⁷ of positive column discharge of mercury in argon at 5 millimeters the electrodes are led out at one end of the tube. Two anodes are separated by a screen and the supply wires of the incandescent oxide cathode are surrounded by insulating envelopes. The tube is widened where the supply wires are taken out for mounting in a device for irradiating flowing substances. A quartz tube with graded seal is employed. In another form,²⁸ the operating current density is maintained so low, either by use of a suitable voltage and a resistance in series with the discharge, or by the use of a suitable gas filling, *e.g.*, argon, that the temperature of the tube is below 100°, and the vapor of the mercury contained in the tube is less than 0.3 millimeter pressure. A lamp has been described²⁹ in which the anodes are carbon cylinders with leveled-off ends. An inner concentric quartz tube for irradiation fluids is embodied in the apparatus. To prevent disintegration products of the cathode from settling on the walls, grid-shaped anodes of gauze or parallel wires stretched on a frame are used to attract disintegrating particles without seriously interfering with the passage of the rays.³⁰ Devers³¹ proposed the use of a loose powder of nitrides of boron, zirconium or titanium to reduce the deposition of cathodic materials on the walls and to react with any trace of water vapor present. A device embodying a reflecting mirror of chromium on the inner wall of the tube is due to Zecher.³² Reynolds³³ described an apparatus in which a high-tension discharge in mercury vapor in argon or neon occurs in a quartz tube free from external protuberances, which is to be immersed in the substance to be irradiated. There is an electrode at one end of a tube with a lead-in wire fused to another tube situated concentrically within the outer tube and fused to the latter. One electrode is of mercury, the other of tungsten or steel. The whole high-tension discharge is symmetrically placed and the radiations pass through only a single thickness of quartz.³⁴

Garrett³⁵ described a glow lamp for ultraviolet radiation for clinical or household use operated on 110-220 volt alternating or direct current without auxiliary equipment. The radiations are emitted by a polyatomic gas such as nitrogen at 2-3 millimeters pressure in admixture with argon, neon and helium at 1-2 centimeters. It was stated that the monatomic gases alter the spectrum of the nitrogen, increasing the proportion of ultraviolet. The monatomic gases also function in starting the discharge and in keeping the operating potential relatively low. Con-

²⁶ See also Lederer, K. and E., German P. 600,757, July 31, 1934.

²⁷ N. V. Philips' Gloeilampenfabrik, British P. 320,358, October 9, 1928; French P. 662,717, October 20, 1928; *Chem. Abs.*, **24**, 270 (1930).

²⁸ British P. 299,704, October 22, 1928; N. V. Philips' Gloeilampenfabrik; *Brit. Chem. Abs.*, **B**, 246 (1930).

²⁹ British P. 299,931, November 8, 1928, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **23**, 3379 (1929).

³⁰ British P. 351,894, July 2, 1931, N. V. Philips' Gloeilampenfabrieken.

³¹ Devers, P. K., U. S. P., 1,803,175, April 28, 1931.

³² Zecher, G., U. S. P. 1,951,116, March 13, 1934; *Chem. Abs.*, **28**, 3279 (1934). See also British P. 381,084, September 29, 1932; 366,675, February 11, 1932, to Philips Lamp Works.

³³ Reynolds, F., British P. 349,294, May 28, 1931.

³⁴ Many variations have been described. See, *e.g.*, Braselton, C. H., Ruben, S., Davies, L., and Harding, R., for a series of patents, U. S. P. 2,007,919-47, July 9, 1935, to Sirian Lamp Co.; Freedman, P., British P. 313,726-7, 1929; Geffcken, H., and Richter, H., British P. 265,636, May 3, 1928; Studienges. für Wirtschaft und Industrie, British P. 269,808, 1926; Kewley, F. E., and Balls, S. F., British P. 269,014, June 14, 1926. Even carbon electrodes have been proposed, British P. 410,706, 1934.

³⁵ Garrett, M. W., U. S. P. 1,783,643, Dec. 2, 1930, to Westinghouse Lamp Co.

centric grid-shaped electrodes of tungsten or molybdenum are employed in a quartz envelope, which contains also a strongly electropositive metal, alkali or alkaline-earth, which deposits on the electrodes and makes the lamp suitable for operation at 110 volts. Mercury may also be used in the lamp.

A low-pressure mercury glow-discharge lamp, employing indirectly-heated unipotential oxide-coated electrodes as the source of electron emission to ionize the mercury vapor has been described by Marden and Nicholson³⁶ of the Westinghouse Co. It is necessary to use a transformer or a ballast lamp with the glow lamp to avoid overheating the electrodes. The voltage across the terminals of the glow lamp, and the resultant heating of the electrodes, decrease to a certain extent with increasing glow current, making the device self-regulating. The electrodes serve alternately as anodes and cathodes when used on alternating current. Such lamps have been made in sizes from those taking 0.2 to 0.3 ampere in half-inch bulbs one inch long to 30-ampere models in bulbs 3 to 12 inches in diameter. Figure 71 shows

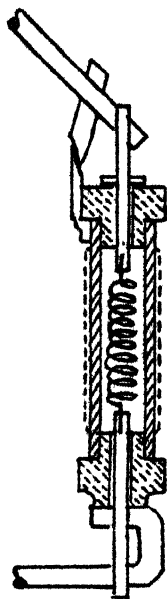


FIGURE 71 (Left).

Structure of Indirectly Heated Electrode of Marden and Nicolson. (*Transactions Illuminating Engineering Society*).

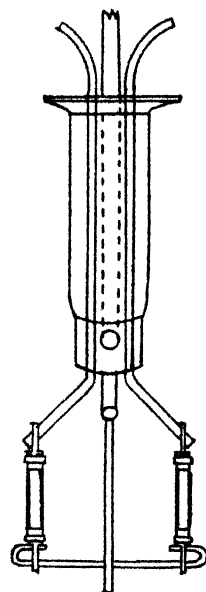


FIGURE 72 (Right).

Construction of Assembled Mount (*Transactions Illuminating Engineering Society*).

the indirectly heated electrodes and Figure 72 their mounting. The electrode around each heating coil is connected to the same lead-in wire as its respective coil. When the glow lamp is in series with a tungsten filament or other ballast on a 115-volt alternating current circuit, the voltage across the lamp is about 40 volts, until the electrodes are heated sufficiently to emit. During three to five seconds, the emission and glow-discharge increase and the lamp voltage drops to a point where the heating of the electrodes by the coils and by electronic and ionic bombardment maintains sufficient emission from the electrodes to sustain the glow-discharge current. During steady operation, about one-half of the current passes through the heater coils and the remainder is glow current. Marden and Nicholson gave data obtained with

³⁶Marden, J. W., and Nicholson, M. G., *Trans. Illum. Eng. Soc.*, 26, 592 (1931); British P. 374,466, May 21, 1930; *Chem. Abs.*, 27, 3152 (1933).

a monochromator (uncorrected for reflection and absorption) comparing the energy distribution of the new glow lamp with those of the quartz mercury arc and the S-1 lamp. The percentage distribution of energy for the Corex glow lamp is about the same as for the mercury arc, except at the lower wave-lengths where the Corex glass absorbs the radiations. (See Chapter 10.) Of the total ultraviolet output, 90 per cent lies between 3132 and 2894Å. On the other hand, Inman stated that, even through Corex, this glow lamp emits an amount of energy of the 2537Å line which is undesirable for long-continued use. He believed that attempts to eliminate this would make the output between 2800 and 3100Å negligible. Luckiesh pointed out that the S-1 lamp (see section on "dual-purpose" lighting) emits less of the 2537 line, since it operates under a higher pressure of mercury vapor.

Increasing the temperature or adding other gases such as argon concentrates the glow and diminishes the ultraviolet output. One, two, or possibly more of the lamps may be operated in series with a ballast which may be either a tungsten-filament lamp, an infrared heater, a choke coil, or a special transformer which can be concealed in a table lamp fixture.

Marden and Rentschler³⁷ claimed an improvement in the Marden glow lamp by making the heat-radiating capacity of the device great enough to maintain the internal temperatures between 20° and 75°C. The mercury reservoir is placed in a protuberance, with a more or less restricted opening, giving but a limited exposure of the mercury to the heat. This limits the mercury vapor pressure to 0.001-0.08 millimeter, which makes the emission of the 2537Å line ten times as strong as the other lines. This point has also been emphasized by the Philips Lamp Works.³⁸ The desirability of increasing the output of this line obviously depends upon the purpose to which the lamp is to be put, a matter which will receive attention in subsequent parts of this book.

Prouty³⁹ described a portable compact power system including transformers, milliammeters, etc., for operating several quartz discharge tubes at high voltages and low currents (30-50 milliamperes). The tubes are of small diameter to reduce self-absorption of the resonance lines and yield intense short-wave ultraviolet radiations stated to be applicable for dental and surgical utilization.

Ultraviolet-emitting discharge tubes of quartz employing other emitting metals than mercury have been produced; sodium and magnesium have been proposed. Magnesium tends to impair the transparency of the tube. The Philips Works⁴⁰ proposed to preserve the transparency of the walls by coating that part of the wall intended for the passage of the rays with a substance (potassium chloride or fluoride or fluoborate in the case of magnesium) which either prevents deposition of the metal or renders the deposit transparent to the rays desired. Calcium fluoride may be used as a coating for the interior of a mercury vapor lamp. When the tube contains sodium vapor, the wall may be coated with sulfur or phosphorus. de Boer⁴¹ places on some non-transmitting part of the bulb, a material which will adsorb the depositing substance and liberate it on heating. Carbon, calcium fluoride or zirconium oxide are suggested. The spectrum is emitted by iodine vapor in this tube.

³⁷ Marden, J. W., and Rentschler, H. C., U. S. P. 1,917,848, July 11, 1933. See also Canadian P. 355,173, Jan. 7, 1936. For more recent developments, see Marden, J. W., and Meister, G., U. S. P. 2,129,357, Sept. 6, 1938; *Chem. Abs.*, 32, 8285 (1938).

³⁸ British P. 299,704, January 16, 1930, to N. V. Philips' Gloeilampenfabrieken.

³⁹ Prouty, W. O., U. S. P. 1,965,947, July 10, 1934; U. S. P. 2,093,735, Sept. 21, 1937; *Chem. Abs.*, 31, 7773 (1937). See also Le Bel, C. J., U. S. P. 2,126,787, Aug. 16, 1938; *Chem. Abs.*, 32, 7836 (1938).

⁴⁰ British P. 336,222, July 5, 1929; 356,407, September 10, 1931; both to N. V. Philips' Gloeilampenfabrik.

⁴¹ de Boer, J. H., U. S. P. 1,935,699, November 21, 1933; *Chem. Abs.*, 28, 693 (1934).

For mercury vapor, gold foil may be used. de Groot and Reerink⁴² employ a member acting as a chimney above the path of discharge to carry off the vapor, which may settle on or combine with the chimney, a part of which is of gauze. This chimney is to be employed in a magnesium vapor lamp.

Tubes have been described in which the emission of ultraviolet radiations is caused by bombardment by electrons of a fluorescent substance on the electrodes or in a very thin film on the inner side of the wall of the quartz tube. Sulfides, selenides, oxides of the alkali or alkaline earth metals, boron compounds, etc., with small amounts of iron or mercury compounds incorporated, serve as emitters. Yttrium, lanthanum and gadolinium compounds increase the emission. The tube has a very low pressure gas or vapor filling. A grid-like anode accelerates the electrons emitted by the cathode. Visible radiations are emitted by the wire of the heater. A chromium or magnalium film on the opposite part of the bulb serves as a mirror.⁴³

Materials within the envelopes of discharge tubes may also be excited by ultraviolet rays within the tubes to give blue or white fluorescent light.⁴⁴ In some of these zinc silicate, calcium tungstate and calcium molybdate form the internal coatings of the envelopes. A series of variously fluorescing layers is sometimes used. Fluorescent glass envelopes may also be employed.⁴⁵ Rare gas fillings⁴⁶ are sometimes used to the exclusion of mercury.⁴⁷

DUAL-PURPOSE SOURCES

The proportion of the health-giving ultraviolet in the sun's radiations is small and varies greatly with the seasons and atmospheric conditions. It is greatly lessened by dust and smoke, so that in industrial communities and in cities very little may be available. Means have been developed for so altering the ordinary sources of illumination of homes, hospitals, schoolrooms, gymnasias, etc., as to enable them to provide also a supply of the desirable ultraviolet radiations. Illumination by such sources has come to be known as "dual-purpose" illumination, *i.e.*, visible illumination and simultaneous ultraviolet irradiation.

The engineering problems are concerned with the design and construction of a reasonably-priced source of ultraviolet within a lamp bulb supplying visible light

⁴² de Groot, W., and Reerink, E. H., U. S. P. 1,905,688, April 25, 1933, to General Electric Co. Hummel, C., British P. 387,130, Feb. 2, 1933; Aicher, J. D., U. S. P. 2,109,984, March 1, 1938; *Chem. Abs.*, 32, 3279 (1938); French P. 828,067, May 10, 1938, to Compagnie des lampes; *Chem. Abs.*, 32, 6962 (1938).

⁴³ British P. 459,323, Jan. 6, 1937; 473,929, Oct. 22, 1937; *Chem. Abs.*, 32, 2854 (1938); German P. 656,213, Feb. 1, 1938; British P. 476,240, Dec. 7, 1937; 485,875, May 26, 1938; *Chem. Abs.*, 32, 8286 (1938), all to Patent-Treuhand-Ges. für elektrische Glühlampen. See also Randall, J. T., British P. 466,503, May 28, 1937; *Chem. Abs.*, 31, 7774 (1937); British P. 469,731-2, July 27, 1937; *Chem. Abs.*, 32, 436 (1938), to General Electric Co., Ltd. Broadner, R. L., Randall, J. T. and Ryde, J. W., British P. 474,298, Oct. 28, 1937; *Chem. Abs.*, 32, 2854 (1938); Randall, J. T., British P. 474,457, Nov. 2, 1937; *Chem. Abs.*, 32, 2854 (1938). Rhodamine dyes may also be used, according to McKeag, A. H., and Randall, J. T., British P. 474,297, Oct. 28, 1937; *Chem. Abs.*, 32, 3279 (1938); Jenkins, H. G., Ryde, J. W., and Wilson, G. H., British P. 483,846, April 27, 1938; *Chem. Abs.*, 32, 6961 (1938); Jenkins, H. G., Canadian P. 375,310, July 26, 1938; *Chem. Abs.*, 32, 6962 (1938); Randall, J. T., Canadian P. 375,308, July 26, 1938; *Chem. Abs.*, 32, 6962 (1938).

⁴⁴ French P. 808,048, Jan. 27, 1937, to Corning Glass Works; *Chem. Abs.*, 31, 6434 (1937); British P. 476,945, Dec. 20, 1937, to I.G. Farbenindustrie, A.-G.; *Chem. Abs.*, 32, 4298 (1938); British P. 484,975, May 12, 1938, to N. V. Philips' Gloeilampenfabriken; *Chem. Abs.*, 32, 8286 (1938).

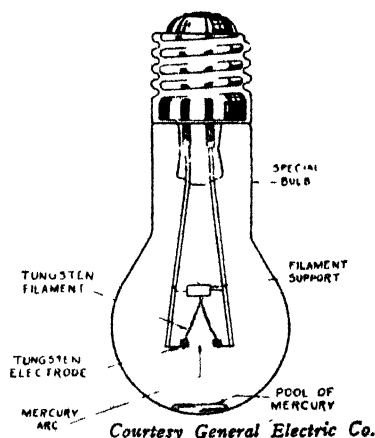
⁴⁵ French P. 810,298, March 18, 1937; *Chem. Abs.*, 31, 8384 (1937); British P. 474,907, Nov. 9, 1937; *Chem. Abs.*, 32, 3280 (1938); French P. 822,815, Jan. 8, 1938; British P. 457,317; *Chem. Abs.*, 31, 2946 (1937); all to Soc. anon. pour les applications de l'électricité et des gaz rares-etablissemments Claude-Paz and Silva. Laise, C. A., U. S. P. 2,116,977, May 10, 1938; *Chem. Abs.*, 32, 4892 (1938); Fritze, O., Rüttenauer, A., and Wiegand, K., U. S. P. 2,103,032, Dec. 21, 1937; *Chem. Abs.*, 32, 1193 (1938).

⁴⁷ For general discussions of this new type of fluorescent lighting which has the advantage of simulating daylight, see Claude, G., *Compt. rend.*, 203, 1203 (1936); Servigne, M., *Ibid.*, 1247; Harrison, W., and Hibben, S. G., *Elec. World.*, 109, 1530 (1938); Inman, G. E., and Thayer, R. N., *Elec. Eng.*, 57, 245 (1938); von Ardenne, M., *Z. tech. Physik*, 19, 41 (1938); Hibben, S. G., *Elec. J.*, 35, 269 (1938).

and capable of operating from an ordinary lamp socket without the necessity of elaborate or expensive accessory equipment. From a therapeutic standpoint, the questions of wave-length range and intensity are paramount. It is necessary to choose for the envelope of the lamp bulb a material which will transmit visible light and ultraviolet radiations longer than about 2900 to 3000A and absorb those shorter than this limit, since the shorter rays are known to exhibit deleterious effects. As it is well known that excessive exposure to the sun's ultraviolet transmitted by the earth's atmosphere (longer than about 2950 to 3000A) may be harmful, it is necessary that the ultraviolet radiations emitted by a "dual-purpose" lamp be low in intensity since the lamps are used for considerable periods in ordinary home illumination. This explains the otherwise paradoxical nature of the claims of certain manufacturers that their bulbs emit only very low intensities of ultraviolet. A considerable field remains to be explored in order that the most suitable intensities and wave-length regions for effecting desired therapeutic ends may be firmly established. It is important that exact data be acquired regarding the effects of prolonged exposures to low intensities of the therapeutic range of the ultraviolet. Comparatively small amounts seem to be needed, at least for the prevention of rickets in chickens.⁴⁸ An industrial Cooper-Hewitt arc in glass affords some antirachitic protection, although not as much as one in Corex D glass, which, in turn, is somewhat less effective than one in quartz. Even 60- or 500-watt Mazda CX lamps, which have only a small ultraviolet output, have been recommended for long-continued use in poultry houses.⁴⁹

FIGURE 73.

Sunlight (Type S-1) Lamp.



One of the first bulbs for "dual-purpose" lighting was the S-1 sunlamp.⁵⁰ It comprises a combination of a mercury arc in argon between tungsten electrodes and an incandescent tungsten lamp in the same bulb, the latter of special glass of low iron content to transmit radiations from 2800 to 3100A.⁵¹ Figure 73 shows the

⁴⁸ Hughes, J. S., and others, [Trans. Ill. Eng. Soc., April, 1927]; cited by Buttolph, L. J., Trans. Ill. Eng. Soc., 26, 583 (1931).

⁴⁹ Anon., Trans. Ill. Eng. Soc., 26, 551 (1931).

⁵⁰ Luckiesh, M., Gen. Electric Rev., 33, 89 (1930); Forsythe, W. E., et. al., Gen. Elec. Rev., 33, 358 (1930); Luckiesh, M., Elec. World, 94, 835 (1929); 95, 300 (1930); Trans. Ill. Eng. Soc., 25, 397 (1930); Gordon, N. T., and Benford, F., Gen. Elec. Rev., 33, 283 (1930); Forsythe, W. E., and Christison, F., Ibid., 32, 662 (1929).

⁵¹ Strickland, R. F., British P. 147,292, 317,832, 375,477 (1932), to British Thomson-Houston Co., Ltd. Strickland, F., Blake, H. D., and McLean, S., British P. 398,290, September 14, 1933. See also British P. 383,342, November 17, 1932, to Zaidan-Hojin Aoyagi Kenkyusho, for a method of starting a similar lamp.

structures within the bulb. No tilting is required to start this lamp. When the filament is lighted, the arc strikes across the filament terminals and disposes itself across the main electrodes. A wide range of operating angles is possible. A low-voltage supplied by a transformer with a special volt-ampere characteristic is essential to the operation of this lamp, which consumes approximately 400 watts. The no-load voltage of the secondary of the transformer is approximately 35. When the switch is closed, the filament takes about 9 amperes and the drop across it is about 33 volts. The mercury arc starts in parallel, the voltage drops to eleven volts, and the total current through both arc and filament is 30 amperes. In operation, the arc supplies about one-fourth of the light, two-thirds coming from the tungsten electrodes, the color temperature of which is above 3500°K. The lamp is said to be twenty times more effective than summer sunlight. A frosted bulb is used, and the coiled filament is inverted and located above the electrodes. In another model, S-2, the arc length is increased, and a metal cap of aluminum is placed over the lower portion of the bulb to minimize glare and to redirect much energy back into the mercury vapor area, increasing the operating temperature. As a result, the lamp emits about one-half as much ultraviolet as the S-1 model, while consuming only 40 per cent as much energy. The lives of the S-1 and S-2 lamps are shortened by both over- and under-voltage operation.⁵² Porter, Egeler and Sturrock⁵³ have tabulated electrical and other physical data regarding these sources. Luckiesh has pointed out that the high mercury-vapor pressure of these lamps leads to a high degree of absorption of the 2537Å line, long-continued exposure to which would be dangerous.

The spectrum emitted by the tungsten-mercury arc, according to Forsythe and Easley,⁵⁴ shows a continuous radiation from 4000 to 2100Å. When the temperature is increased by external heating, the increased mercury vapor pressure causes the mercury absorption bands to appear. The 2540 band is 0.1Å wide at 220°C. (vapor pressure 32 mm.) and with increasing temperature spreads to longer wave-lengths, reaching 2576Å at 407°, and 2652Å at 426°C. At 350°C., the resonance line disappears, being replaced by two narrow bands at 2534 and 2532Å which at higher temperatures merge with the 2540Å band. At 426°C., there is continuous absorption between 2530 and 2652Å, with evidence of further absorption beyond 2652Å. Five fluted bands around 2345Å appear between 320° and 340°C. and broaden until they cover 16Å at 420°C. Pressure causes the disappearance of some lines between 3500 and 2100Å. These effects are somewhat different from those exhibited by mercury vapor in an absorption cell.

During the first few seconds of operation, the S-1 lamp emits some argon lines, but after a few minutes only mercury lines are detected.⁵⁵ Similar effects are observed if the argon is replaced by helium neon, nitrogen or carbon dioxide. When hydrogen is the gas present, the lamp continues to radiate bands characteristic of mercury hydride, along with several other bands at shorter wave-lengths.

Other data on the radiations emitted by the General Electric Sunlamp have been published by Benford,⁵⁶ Coblentz⁵⁷ and Barnes.⁵⁸ Barnes gave the average energy flux values of a number of lamps for the principal mercury lines between 2500 and

⁵² Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, **28**, 121 (1933).

⁵³ Porter, L. C., Egeler, C. E., and Sturrock, W., *Trans. Ill. Eng. Soc.*, **27**, 23 (1932).

⁵⁴ Forsythe, W. E., and Easley, M. A., *Phys. Rev.*, **36**, 150 (1930).

⁵⁵ Dooley, D., *Phys. Rev.*, **36**, 1476 (1930).

⁵⁶ Benford, F., *J. Motion Picture Eng.*, **14**, 414 (1930); Gordon, N. T., and Benford, F., *Gen. Electric Rev.*, **33**, 290 (1930).

⁵⁷ Coblentz, W. W., *J. Am. Med. Assn.*, **95**, 411 (1930).

⁵⁸ Barnes, B. T., *Phys. Rev.*, **36**, 1468 (1930).

6000A, and for the continuous spectrum up to 17,000A, determined by thermopiles and galvanometer, with a quartz prism monochromator which received on its slit energy from all parts of the arc and the electrodes. The line and continuous emissions were separated by taking readings both at the lines and at intermediate points, plotting continuous curves from the latter, and deducting the continuous curves from the values taken at the lines. The continuous curve was possibly too high below 4500A because of the inclusion of less important mercury lines, while the opposite was true in the red and infrared regions.

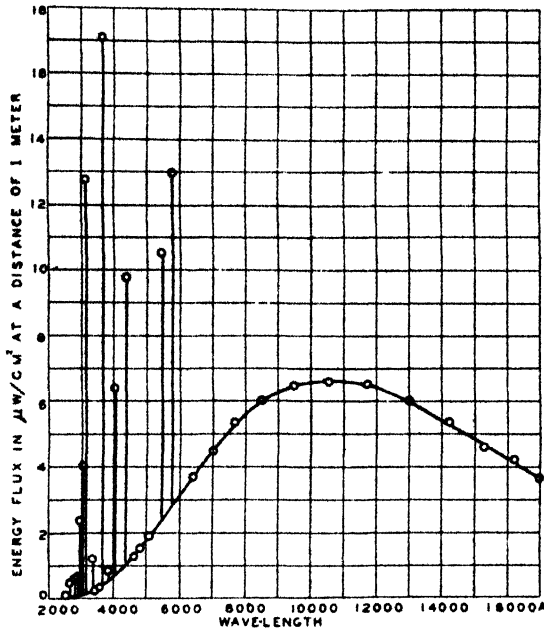


FIGURE 74. Energy Flux ($\mu\text{w}/\text{cm}^2$) One Meter from Center of Arc (General Electric Sunlamp) in a Direction Normal to the Plane of the Leads. Lamp burning without reflector with 115 volts on the primary of the transformer. Average lamp current and voltage 30.9 amps and 10.6 volts. Curve represents energy in 50Å band of continuous spectrum. Heavy lines above the curve give energy flux in lines or groups of lines in arc spectrum (B. T. Barnes, *Physical Review*).

In Figure 74 the intensities in microwatts per square centimeter at one meter distance in a direction perpendicular to the plane of the leads are given for an average of 26 lamps, operated with 115 volts on the primary of the transformer. The peak of the curve lies at about 10,600A, quite close to the maximum in the curve for the energy radiated by tungsten at 2500°K. The shape of the curve below 5000A, however, is approximately that for tungsten at 3250°K., the temperature of the hottest parts of the electrodes. The output of visible and ultraviolet radiations was much too high in comparison with that of the infrared for tungsten at 2500°K., a fact explained by the composite nature of the continuous radiation, the electrodes (above 3000°K.) giving a relatively high proportion of visible and ultraviolet, while the filament and the incandescent parts of the leads at much lower temperatures,

but with a larger area, give much of the infrared, and shift the maximum to longer wave-lengths.

The average total energy flux at one meter is 2380 microwatts per square centimeter (10.6 volts and 30.95 amperes). Table 13 gives the average energy flux for each of the principal mercury lines, and the corresponding per cent of the average total energy flux.

Table 13.—Energy Flux of Mercury Lines.

Wave-length of line, Å	Microwatts per cm. ²	% of total	Wave-length of line, Å	Microwatts per cm. ²	% of total
5780	9.7	0.4	3130	13.8	0.57
5461	8.2	0.34	3024	4.4	0.18
4358	9.0	0.38	2967	2.5	0.107
4047	5.0	0.21	2894	0.71	0.030
3905	0.4	0.017	2804	0.6	0.025
3650	17.4	0.73	2650	0.68	0.027
3342	1.1	0.046	2537	0.11	0.004

The distribution between line and continuous spectral energy in various broad wave-length regions is given in Table 14.

Table 14.—Distribution Between Line and Continuous Spectral Energy.

Microwatts per cm. ²	2500-3200Å	3200-4000Å	4000-7600Å	7600-17,000Å	17,000Å
Line spectrum	22.0	18.0	(32.7)*
Continuous	0.6	5.2	209.
Both	23.6	24.1	242.	1090	1000

* Red lines in the mercury spectrum included with the continuous spectrum

The continuous spectrum furnishes less than 3 per cent of the energy below 3200Å, but over 86 per cent of the visible. Since much of the continuous spectrum is in the red end with low visibility, the continuous spectrum furnishes only 76 per cent of the light radiated perpendicular to the plane of the leads. Of the total, one per cent is radiation of wave-length less than 3200Å, one per cent is between 3200 and 4000Å, and 10 per cent lies in the visible. That less than 3000Å is only 3 per cent of the total emitted energy.

The results are in fair agreement with those of Benford, although the compositions of the bulbs have been changed. Different lamps vary widely in regard to the emission of the 3650Å line, the intensity of which often increases over 50 per cent during the first 40 hours of burning. Benford found 28 per cent higher values for the energy between 4000 and 7000Å (185 microwatts per square centimeter), a divergence for which no explanation could be given. The results are not comparable with those of Coblenz whose measurements were made upon the whole lamp unit, including a reflector. Under these conditions, the temperature of the mercury pool is 7° higher and the output below 3200Å might be expected to be 10 to 15 per cent greater.

There have been other types of lamps proposed for "dual-purpose" lighting. The bulb of Corex (or Pyrex) may contain a mercury globule and oxide-coated electrodes to produce the ultraviolet-emitting glow discharge that fills the bulb at low temperature, while a sealed inner bulb provided with a tungsten filament serves both as a ballast resistance for the mercury vapor discharge and as a source of light.⁵⁹

⁵⁹ Luman, G. E., British P. 390,384, April 6, 1933, to British Thomson-Houston Co., Ltd.

⁶⁰ Goeterhuis, E., U. S. P. 1,951,106, March 13, 1934, to General Electric Co. See also Craig, P., U. S. P. 1,798,658, March 31, 1931.

Oosterhuis⁶⁰ has described a reading lamp, with a standard containing the necessary transformers, which may comprise a helically wound glower for infrared and visible light, ultraviolet being supplied by a discharge between an incandescent cathode and two anodes in argon at a few millimeters, the tube containing some liquid mercury. The two sources employ separate circuits, each with a transformer, and are usable independently. Sperti⁶¹ placed the arc and the filament in separate chambers.

Other attempts to produce "dual-purpose" illumination include utilization of a combination of separate quartz mercury arcs of usual form, and lamps for visible light in one fixture, provided with reflectors, filtering windows, and provisions for ventilation.⁶² There has also been a considerable development of reflectors and accessory fixtures for the application of the S-1 Sunlamp. Oxidized or polished aluminum and polished chromium are among the more effective reflecting materials for ultraviolet between 2800 and 3200Å.⁶³ Details of installations for homes, schools, offices, gymnasias, swimming pools, etc., have been described.⁶⁴

METALLIC VAPOR ARCS OTHER THAN THE MERCURY TYPE

The dependence of the intensity and efficiency of radiation in metal vapors on pressure is similar for mercury, cadmium and zinc.⁶⁵ At the time of the development of the mercury-vapor arc, Stark and Küch⁶⁶ examined Heraeus quartz lamps

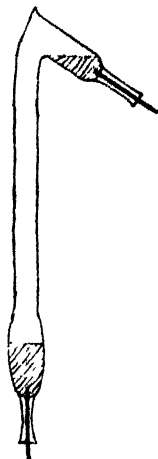


FIGURE 75.

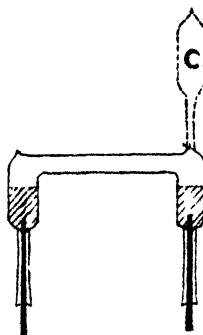


FIGURE 76.

having electrodes of metals and metalloids. The lamps were made in both of the forms indicated by Figures 75 and 76. Most of these lamps are of little practical interest because of the difficulty of starting, although developments of the cadmium

⁶¹ Sperti, G., British P. 396,210, August 3, 1933.

⁶² Rolph, F. W., U. S. P. 1,945,567, February 6, 1934, to Holophane Co. Paget, R. A. S., U. S. P. 1,943,877, January 16, 1934, to Thermal Syndicate.

⁶³ Coblenz, W. W., and Stair, R., *Bureau Standards J. Res.*, 4, 189 (1930); Luckiesh, M., and Taylor, A. H., quoted by Porter, L. C., Egeler, C. E., and Sturrock, W., *Trans. Ill. Eng. Soc.*, 27, 30 (1932).

⁶⁴ Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, 28, 121 (1933).

⁶⁵ Fabrikant, V. A., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat. Ser. phys.*, 441 (1936); *Chem. Abstr.*, 31, 2925 (1937).

⁶⁶ Stark, J., and Küch, R., *Physik. Z.*, 6, 438 (1905).

arc have excited interest. The outer diameter was 0.9 centimeter, the length of the form shown in Figure 75 was 13 centimeters and of that shown in Figure 76 was 9 centimeters. Nickel rods served to conduct the current to anode and cathode. The lamp was charged with metal by means of the container C shown in Figure 76. This container was filled with molten metal and on evacuation of the tube the metal passed into the lamp tube, after which the container C could be removed by fusing the narrow part. The lamp was pumped out thoroughly while in operation in order to get a satisfactory vacuum. The lamp was started by a spark from an induction coil, the metal being heated by a gas blast-lamp until sufficient metal vapors had been produced to cause an arc to form. A voltage of 100-200 was used.

The cadmium lamp was easy to start and operated at 2 to 5 amperes with metal-cooling; with water-cooling it could be operated at 8 amperes. The zinc lamp was more difficult to start and required heating with a blast lamp in order to put it into operation. With metal-cooling it operated at 3 to 5 amperes. The lead lamp required very intense heating in order to start. With water-cooling it operated at 8 to 10 amperes producing a strikingly rich spectrum. The bismuth lamp also

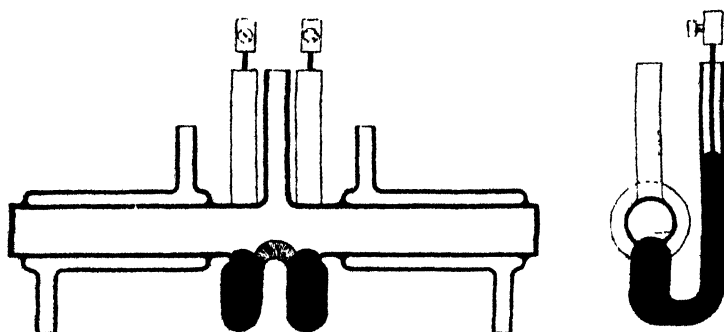


FIGURE 77. Cadmium Lamp.

required intense heating when starting and with water-cooling could be run at 7 amperes. The antimony lamp on the contrary was easily lighted and burned at 3 amperes, and did not require water-cooling unless a very strong current was employed. The spectrum covered a very wide range so that bodies exposed to the light from this lamp more nearly resembled their normal daylight color than when mercury or similar metallic arcs were employed. The antimony arc gave rise to very strong fluorescent effects, sodium glass fluorescing strikingly with a greenish-yellow color, while lead glass exhibited a blue fluorescence. Tellurium and selenium lamps were also tested. The former was operated at 6 amperes. The selenium lamp offered difficulties in starting. A form of cadmium arc lamp, that of Lowry and Abram,⁶⁷ shown in Figure 77 maintains the arc between water-cooled electrodes of solid cadmium. This cooling is important, partly because it checks the vaporization of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped.

The lamp is operated in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and this gas must be pumped off in order to maintain the vacuum. Occasionally, when the

⁶⁷ Lowry, T. M., and Abram, H. H., *Trans. Faraday Soc.*, 10, 103. Note Bates, F. J., *Phil. Mag.*, 39, 353 (1920).

vacuum is good, the arc will start itself on merely switching on the current, but usually it is necessary to start the arc by a spark. This can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In one form of the lamp these windows are protected from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube. The latter must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica is provided to bring the arc to the center of the tube. The cadmium arc will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of cadmium from the electrodes, which thus become shortened unduly.

Stammreich⁶⁸ describes a metallic vapor lamp using cadmium amalgam in which a condenser is connected to the arc tube for collecting metal distilled from the latter. In some instances⁶⁹ mercury may be distilled from the amalgam to a separate compartment which is then closed before the cadmium begins to vaporize. The mercury is afterward run back by tilting the lamp.

Nagaoka and Sugiura⁷⁰ have reviewed the development of cadmium lamps with emphasis on the deficiencies of the previous types. They describe a lamp which comprises a tube with fused quartz cylinder surrounded with molybdenum or tungsten wire, the latter heated by electric current which can be raised to the required temperature. A second fused quartz cylinder is placed above the first cylinder, suspended by a holder which has a hole permitting light to pass through a window placed at the end of the side arm. The cadmium vapor is produced in this cylinder. The luminous particles can be concentrated in a second cylinder to obtain great intensity of light and the density of the cadmium vapor can be controlled by heating the coil around the first cylinder. A cathode of coiled tungsten is used to concentrate electronic currents through the cadmium vapors toward the molybdenum anode. Electric potential of 100 volts and electronic current of 0.3 to 4 amperes between cathode and anode are sufficient to excite cadmium vapors at 300° and to obtain intense and stable light. The tube is constructed of double glass and is water-cooled.

Other cadmium amalgam discharge tubes have been described by the N. V. Philips' Gloeilampenfabriken.⁷¹ Krishnamurti⁷² has found a cadmium-tin alloy arc a suitable source for the excitation of Raman spectra. The lines 5085.8 and 6438.5 Å are particularly effective.

Because of its wider spectral extension in the visible, the cadmium-mercury vapor lamp has attracted much attention for general illumination, but this is not within the province of this book.⁷³

A drawback to the use of cadmium- or zinc-enclosed arcs has been their short-

⁶⁸ Stammreich, H., *British P.* 294,172, July 19, 1927.

⁶⁹ Stammreich, H., *French P.* 657,426, July 11, 1928; *U. S. P.* 1,828,346, October 20, 1931.

⁷⁰ Nagaoka, H., and Sugiura, Y., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **10**, 263 (1929); *Chem. Abs.*, **23**, 5118 (1929).

⁷¹ *British P.* 336,208, July 5, 1929, to N. V. Philips' Gloeilampenfabrieken; Elenbaas, W., *Canadian P.* 371,090, Jan. 11, 1938; *Chem. Abs.*, **32**, 2854 (1938); Elenbaas, W., and Jonas, G. B., *U. S. P.* 2,116,742, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

⁷² Krishnamurti, P., *Indian J. Physics*, **5**, 587 (1930). *Chem. Abs.*, **25**, 1159 (1931).

⁷³ Spanner, H. J., *Trans. Illum. Eng. Soc.*, **30**, 178 (1935); *Chem. Abs.*, **29**, 5359 (1935). For a general discussion of recent electric vapor lamps, see Malley, R. D., *Elec. Eng.*, **53**, 1447 (1934), and Marden, J. W., Beese, N. C., and Meister, G., *Trans. Illum. Eng. Soc.*, **32**, 84 (1937).⁴

ness of life. The metals even when pure tend to adhere to the walls, and break the latter on cooling. Bates⁷⁴ found the addition of a small proportion of gallium to lessen this tendency in the case of cadmium. As he found it difficult to obtain pure gallium, he later employed tin instead, using a 50-per cent alloy of cadmium and tin, which melted at 176-200°C.⁷⁵ The arc used was of the Cooper-Hewitt type; the low vapor-pressure of the tin made the light almost entirely that of cadmium. It has since been stated that the gallium exerted its beneficial effects by virtue of its own impurities. Bismuth, lead or thallium are also effective, but should be limited to less than 1 per cent of the total filling.⁷⁶ The deterioration of the quartz envelopes of high-pressure lamps has been ascribed to attack by positive ions of the metal vapor, which have greater chemical activity than the atoms. This deterioration the Siemens-Halske Co.⁷⁷ propose to obviate by covering a part of the wall near the bulb or portion of the arc in which considerable potential drop occurs by an openwork metallic structure of spiral or braid or metal strips placed edgewise and not connected to a source of potential.⁷⁸

A cadmium amalgam arc, especially intended as a source for the preparation of vitamin D,⁷⁹ is designed to avoid breakage on cooling by so arranging that on interruption of the discharge, the tube is automatically put in such a position that the free surface of the substance yielding the vapor is larger than when the lamp is in the working position. Carbon electrodes are used in a lamp employing a discharge in cadmium vapor mixed with nitrogen and hydrogen or a rare gas, and designed for television, the excitation of fluorescence, and for therapy.⁸⁰

The Siemens and Halske Co.⁸¹ proposed to stimulate the growth of plants by a lamp which emits predominantly in the region 3300 to 3600Å. That such rays would prove effective was based upon the claims (by no means generally accepted) of workers with mitogenetic rays that dividing cells give out radiations of wave-length 3400Å. This region was also claimed to be useful for healing purposes because of an alleged destructive action on virulent tumors. That sunlight lacks this property was claimed to be due to an antagonistic action of even low intensities of radiations in the wave-length region 3200 to 2900Å. For the lamp, there was suggested an arc in quartz, one electrode being silver or zinc. The arc was to be drawn out as far as possible by a moving gas jacket. The intensity of the crater was to be reduced by fins or by water-cooling, the light from the center of the arc only being used. A filter for suppressing radiations of wave-lengths less than 3200Å was also employed. Also an arc in vapors from alloys of the zinc group, such as zinc (17 per cent), cadmium (83 per cent) was proposed.⁸²

Mitchell⁸³ compared three methods of securing the resonance lines of cadmium or zinc for use in physical studies of fluorescence. The methods utilized were the high potential discharge in a mixture of helium and zinc vapor,⁸⁴ a discharge tube

⁷⁴ Bates, F., *Bureau Standards Sci. Paper No. 371* (1920).

⁷⁵ Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **50**, 771 (1928).

⁷⁶ British P. 372,843, May 19, 1932, to Siemens and Halske, A.-G.

⁷⁷ British P. 397,680, August 31, 1933, to Siemens and Halske, A.-G.

⁷⁸ For details of the static characteristics of the high-pressure cadmium arc, see British P. 404,341, January 15, 1934, to Siemens and Halske, A.-G.

⁷⁹ British P. 366,366, February 4, 1932, to N. V. Philips' Gloeilampenfabriken. See also Elenbaas, W., and Jonas, G. B., U. S. P. 2,116,742, May 10, 1938, *Chem. Abs.*, **32**, 4891 (1938).

⁸⁰ British P. 418,128, October 18, 1934, to General Electric Co., Ltd., and Patent-Treuhand.

⁸¹ British P. 296,724, February 24, 1930, to Siemens and Halske, A. G. Silver-leaf filters transmitting between 3050 and 3300Å, may be employed in the envelopes, according to C. J. Milner, British P. 485,787, May 25, 1938, to British Thomson-Houston Co.; *Chem. Abs.*, **32**, 7835 (1938).

⁸² British P. 306,112, February 27, 1930, to Siemens & Halske Co.

⁸³ Mitchell, A. C. G., *J. Frank. Inst.*, **212**, 305 (1931).

⁸⁴ Ellett, A., *J. Opt. Soc. Am.*, **10**, 427 (1925).

of the Schüler type⁸⁶ with hollow cathodes, partly filled with zinc and an arc with hot equipotential, oxide-coated cathode; he found the latter to be the most economical and convenient. The arc was formed in a bulb filled with a helium discharge, and enclosed in a furnace with quartz windows, to vaporize a supply of zinc. The zinc lines began to appear at 330°C. At 370°C., the arc constricts and the helium is pumped out.

A xenon lamp has been described as a source of light in the extreme ultraviolet by Harteck and Oppenheimer.⁸⁶ The lamp is said to yield through a fluorite window the resonance lines of xenon at 1469 and 1295Å. It can be operated for several hundred hours.

MANUFACTURE OF QUARTZ PRODUCTS

Two scientific and engineering leaders had the foresight to grasp the industrial possibilities of the large-scale production of fused quartz, Prof. Elihu Thomson of the General Electric Co. at Lynn, Massachusetts, and Sir Richard Paget in England. Under their leadership, the experimental work developed independently in both countries. In England, the latter organized the Thermal Syndicate in 1903, which carried out early development under the direction of Hutton⁸⁷ and Dr. J. F. Bottomley. An account of the early work has been published by Paget.⁸⁸ The Syndicate early made opaque and translucent fused silica by fusion of glassmakers' sand. In 1906, the Silica Syndicate, Ltd., of London, worked patents of Kent and Lacell for the manufacture of transparent quartz glass. Other developments occurred in Germany, where Heraeus extended the work to the production of the tubes of mercury vapor lamps and Voelker founded a company in 1908, and in France where two companies, Le Quartz Fondu and Quartz et Silice have been producing since the war. The remarkable properties of this acid-resistant material, low solubility and low thermal expansion, made it of great importance to chemical and electrical industries and stimulated the large-scale development of the industry.⁸⁹

The advances in America under the direction of Elihu Thomson in the Thomson Research Laboratory of the General Electric Co. at Lynn have been more closely concerned with the production of articles of clear or transparent quartz, for optical apparatus and for the transmission of ultraviolet radiations, the experimental work on which is largely due to Dr. E. R. Berry, P. K. Devers and L. B. Miller, although the opaque or coarser variety has also been developed by Mr. H. L. Watson. An account of the Lynn developments has been given by Dr. Thomson on the occasion of the presentation to him of the Franklin Medal of the Franklin Institute.⁹⁰ General reviews of the recent developments of the industry have been written by Moore⁹¹ and Ibakh.⁹²

⁸⁶ Schüler, H., *Z. Physik*, **35**, 323 (1926).

⁸⁶ Harteck, P., and Oppenheimer, F., *Z. physik. Chem.*, **16B**, 77 (1932); Groth, W., *Z. Elektrochem.*, **42**, 533 (1936).

⁸⁷ Hutton, R. S., *Trans. Am. Electrochem. Soc.*, **51**, 49 (1927).

⁸⁸ Paget, Sir R., *J. Roy. Soc. Arts*, April 4, 1924.

⁸⁹ Winship, W. W., *Trans. Am. Electrochem. Soc.*, **50**, 177 (1926).

⁹⁰ Thomson, E., *J. Frank. Inst.*, September, 1925.

⁹¹ Moore, B., *Chemistry and Industry*, **50**, 671 (1931); *Trans. Ceram. Soc.*, **31**, 217 (1932); **32**, 45 (1933).

⁹² Ibakh, B., *Keram. Steklo*, **8**, No. 8, 9 (1932) (Russian developments); *Chem. Abs.*, **27**, 821 (1933).

Chapter 9

Sources of Continuous Ultraviolet Radiations for Absorption Studies

In the measurement of ultraviolet absorption spectra, it is desirable that the source of illumination be continuous, or if that condition cannot be attained, the source should at least give a great number of closely spaced lines, so that there may be radiations of practically all wave-lengths available for absorption in the region studied. It is readily apparent that it would be futile to attempt to obtain the fine structure of an absorption band with the mercury arc as a source, since there are wide gaps in which no observations could be made.

One method of attaining this object would be to utilize as electrodes a number of metals, each of which emits many lines. The nature and amounts of the metals should be so chosen that gaps in the spectrum of one are filled by lines from the others. Such a source has been developed for the visible region.¹ The lines are not only closely spaced but are of very nearly equal intensity, so that the weaker ones can be photographed without overexposing the stronger ones. The electrodes are of carbon coated over with a fused mixture of the oxides of vanadium, titanium and molybdenum. The method is not, however, available as yet in the ultraviolet region. For measuring the broad fused systems of absorption bands of substances in condensed systems, that is, of liquids or of solutions, especially where a very high degree of quantitative accuracy is not required, the source of the ultraviolet radiations may be either the iron or the tungsten spark, both of which have many lines. Where it is desired to bring out the finer structure of the absorption bands, particularly in the case of gases, recourse is had to underwater sparks, to incandescent filament lamps burned at high voltage, to cathode-ray bombardment lamps, or to the hydrogen discharge tube.

Underwater Sparks. It has long been known that an arc can be made to burn and that sparks can be passed under liquids. In 1851, Masson² found the under-liquid arc to emit chiefly a continuous spectrum, although in the case of many metals, it has since been shown that there is superposed upon the continuous spectrum a bright-line spectrum. The underwater sparks from a large induction coil, between many metals, were studied by Wilsing,³ who observed that some of the lines were reversed, that is, wholly dark, or bright but marked by a darkened center. The reversals are due to the absorption of emitted radiations by some of the metal vapor or by colloidal metal dispersed in the water. Being excited when dispersed, the atoms are in a condition to absorb many lines. The study of these reversals has been an aid in the classification of the lines of various metals.⁴ Arcing or

¹ Eppley, M., *J. Frank. Inst.*, 201, 233 (1926). Some of the new fluorescent lamps discussed in Chapter 8 may be of value as spectroscopic continuous sources for the visible and longer wave-lengths of the ultraviolet. Servigne, M., and Vassy, E., *Rcv. optique*, 16, 423 (1937); *Chem. Abs.*, 32, 6154 (1938).

² Masson, M. A., *Ann. chim. phys.*, 31, 295 (1851).

³ Wilsing, J., *Astrophys. J.*, 10, 113 (1899).

⁴ Baly, E. C. C., "Spectroscopy," II, 128, London, Longmans, Green (1927).

sparking metals under liquids is one of the standard methods of dispersing the metals to form colloidal suspensions. Because of the turbidity thus produced, an arrangement for circulating the water must usually be provided when the underwater spark is employed as a source for absorption spectrophotography.

Among the first to employ the continuous spectrum emitted under water as a source for the study of the fine structure of absorption bands were Henri and de Laszlo.⁵ Two condensers, each of 2.3×10^{-3} microfarad capacity, were connected in parallel and charged by a transformer supplied with a primary current of 20 amperes at 60 volts, interrupted 600 times a second. There was an auxiliary air spark gap of 15-20 millimeters and an underwater spark between rods of aluminum or copper. The spark was placed 5 centimeters below the surface and at a distance of 10-15 millimeters from a quartz window. The frequency of the oscillatory discharge was found to be of the order of one million per second. The spark was fairly uniform. An exposure of three to five minutes gave a continuous spectrum extending as far as 2100A.

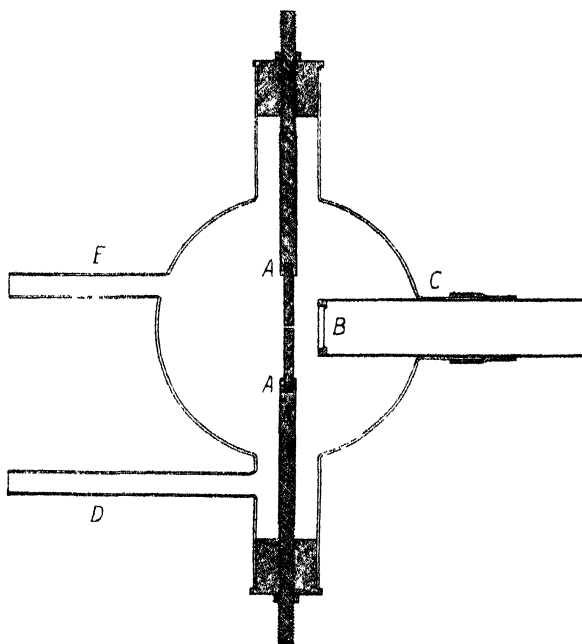


FIGURE 78.

Howe⁶ and later Strachan⁷ used brass electrodes, with 4 to 6 kw. in the primary of the transformer and secured a very satisfactory continuous spectrum extending to 2200A. Fulweiler and Barnes⁸ omitted the Tesla coil and employed the arrangement shown in Figure 78.

⁵ Henri, V., and de Laszlo, H. G., *Proc. Roy. Soc.*, 105A, 668 (1924).

⁶ Howe, H. E., *Phys. Rev.*, 8, 674 (1916).

⁷ Strachan, E. K., unpublished communication to Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, 194, 84 (1922).

⁸ Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, 194, 83 (1922).

The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These were mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the side tubes of a "Pyrex" glass bulb of about 500 cc. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. Fulweiler and Barnes found under the electrical conditions used that a

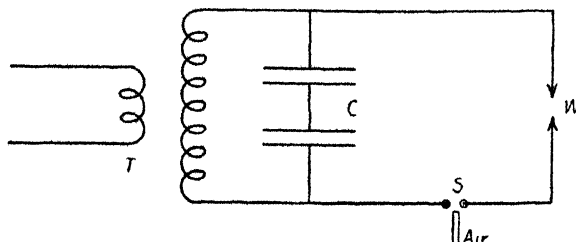


FIGURE 79.

spark length of about 0.5 mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E. For the production of the spark, Fulweiler and Barnes employed a G.E. x-ray transformer, type K, using 15 amperes from the 110 volt a.c. mains on the primary coil. A mercury interrupter which made and broke a d.c. current about 120 times a second was also employed. For capacity, two Leyden jars of about 0.001 mfd. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Figure 79 shows this electrical circuit where T is the trans-

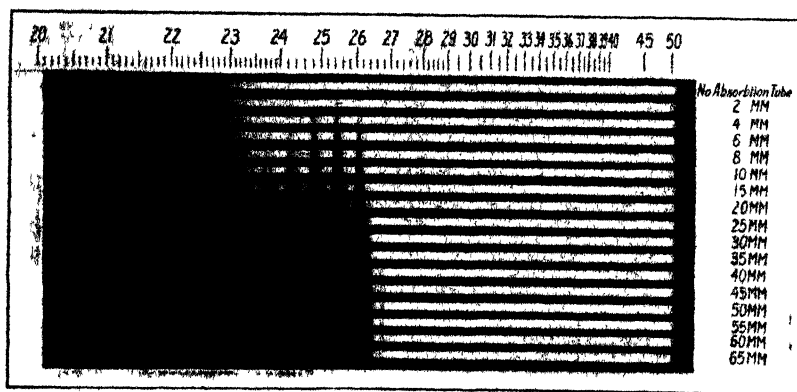


FIGURE 80.

former; C, the capacity; S, the external spark gap and W, the tungsten spark. The choice of tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon, tungsten and molybdenum. The tungsten gave more rays in the shorter wave-lengths and required very much less adjustment. Using 1.6

kilowatts in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. Figure 80 illustrates the continuity of the spectrum thus obtained. The absorption bands are those of a 0.1-per cent solution of benzene in ethyl alcohol. The lengths of the solution used are indicated on the side of the plate. This photograph was taken with a Hilger quartz spectrograph. The top exposure with no absorption tube indicates the uniformity of the irradiation. In the original negative the spectrum extends to 2050A.

Snyder⁹ employed a Tesla spark maintained under water, and utilized especially designed holders for the electrodes. Allin¹⁰ found the uranium spark under water to give a perfectly continuous, intense spectrum with neither absorption nor emission lines. McNicholas¹¹ employs spark terminals of tungsten (with about a 16 millimeter gap) enclosed in an ebonite box through which a stream of distilled water is circulated. The adjustment and centering of the spark is accomplished by external controls. Lewis¹² has compared ductile uranium, tungsten-steel and aluminum as electrode materials for the underwater spark.¹³

The theory of the continuous nature of the underwater spark in relation to black body radiation has awakened some interest. Wilson¹⁴ has calculated from the position of the intensity maximum of the OH absorption bands in some spark spectra that the effective temperature of the underwater spark is 5115°. Wyneken¹⁵ determined the energy distribution of the underwater spark between aluminum electrodes by photographic-photometric comparison with the known energy distribution of the carbon arc. A definite maximum occurs at 2850A, (with aluminum electrodes) where the intensity is approximately three and one-half times as great as it is in the neighborhood of 4500A. The position of the maximum would indicate, if the radiation were purely thermal, a temperature of 10,000°K. The experimental curve was, however, much steeper than the theoretical black-body radiation curve for this temperature. Substitution of copper electrodes gave no indication that the curve depends on the electrode material. The falling off of the curve in the extreme ultraviolet was not regarded as due to absorption by the water. Very similar results were reported by Wrede.¹⁶ An increase in the energy of the discharge displaces the maximum intensity towards shorter wave-lengths in conformity, in the case of zinc, with Wien's law for temperature radiation. For smaller discharge energy, the temperature of the spark was calculated to be of the order of 7500°K. and for greater energy 10,000°K. In the case of aluminum and magnesium the shift with increasing energy of discharge was less marked than with zinc, cadmium, copper, lead or tin. The temperatures so determined refer to the inner part of the spark, while the much lower temperature found by Wilson probably refers to the mantle surrounding the spark, since his determination was made by calculation from the maximum absorption of a band spectrum. By this method, Stücklen¹⁷ calculated the temperature of the absorbing OH mantle around the underwater copper spark to be 3000°Abs.

⁹ Snyder, V. D., *J. Am. Chem. Soc.*, **49**, 2510 (1927).

¹⁰ Allin, E. J., *Trans. Roy. Soc. Canada*, **21**, Section 3, 231 (1927).

¹¹ McNicholas, H. J., *Bureau Standards J. Research*, **1**, 939 (1928). Details of construction also are given.

¹² Lewis, S. J., *Chemistry and Industry*, 464, 1933.

¹³ See also Tyndall, E. P. T., *Bureau Standards Tech. Paper*, 148 (1920), appendix

¹⁴ Wilson, E. D., *J. Opt. Soc. Am.*, **17**, 37 (1928).

¹⁵ Wyneken, I., *Ann. Physik*, **86**, 1071 (1928)

¹⁶ Wrede, B., *Ann. Physik*, **3**, 823 (1929).

¹⁷ Stücklen, H., *Naturwiss.*, **18**, 248 (1930).

Incandescent Sources. Cohn and Andresen-Kraft¹⁸ suggested as a continuous source for absorption work, the light from cathode-ray bombardment (either in a gas or high vacuum) of a thorium-layered anode. The spectrum was said to extend from 2200 to 6000A, with a maximum intensity at 4500A. Weingeroff,¹⁹ however, did not believe this source to meet the requirements of a truly continuous spectrum. De Kowalski²⁰ and later Gelhoff²¹ used tungsten lamps at 20 to 30 per cent over-rating. (See Chapter 3.) This method gives a continuous but somewhat expensive source, as the lamps burn out quickly. In lamps intended for such use,²² the filament may be put half as close as usual to the wall, a portion of the latter being of quartz. Weingeroff described a source in which a tungsten cylinder in vacuum, nitrogen or a noble gas is made to glow by an electric current. The Osram Co. produce a tungsten lamp in Uviol glass which operates at 250 volts and 2 amperes, and transmits a continuous spectrum to 2900A.

Hydrogen Discharge Tube. The continuous molecular hydrogen spectrum was first observed by Dove,²³ according to Chalonge and Zé.²⁴ Freeman has traced the history of work on this phenomenon.²⁵ It was shown by Horton and Davies²⁶ that slow-moving electrons in hydrogen produce a continuous spectrum. Lemon,²⁷ using a discharge tube with a Wehnelt cathode, found that by varying the filament temperature, he could get in succession, and almost pure, Balmer lines, the molecular spectrum of hydrogen and the continuous spectrum.²⁸ Carst²⁹ concluded, as did Horton and Davies, that the hydrogen molecule is the carrier of the spectrum, which is distinct from the continuous spectrum which is to be expected at the series limit. The use of the hydrogen discharge tube as a source of continuous ultraviolet radiation was introduced by Tingey and Gerke.³⁰ Their source, however, lacked intensity, and exposures of at least an hour often were necessary.

Gehrcke and Lau³¹ described the structureless nature of radiations emitted between 3300 and 1950A by pure hydrogen in an alternating current discharge in an inside silvered tube. Bonhoeffer and Steiner³² employed this source in the absorption spectrophotometry of hydrogen iodide.

A great impetus to the more general use of the hydrogen discharge came from the work of Bay and Steiner,³³ who increased the intensity by employing an end-on arrangement. Also the current density was made as high as possible by loading the tube heavily. They employed aluminum electrodes extending close to the walls, the electrodes having areas of 300 square centimeters. It was stated that the electrodes could carry as much as 500 milliamperes for a day. To get the current

¹⁸ Cohn, W. M., and Andresen-Kraft, C., *Z. tech. Physik*, 12, 428 (1931); *J. Am. Ceram. Soc.*, 15, 122 (1933).

¹⁹ Weingeroff, M. A., *Physik. Z. Sowj.*, 2, 278 (1932).

²⁰ de Kowalski, J., *Arch. des Sciences*, 37, 265 (1914).

²¹ Gelhoff, G., *Z. tech. Physik*, 1, 224 (1920).

²² British P. 359,712, October 29, 1931, to N. V. Philips' Gloeilampenfabrieken.

²³ Dove, *Pogg. Ann.*, 104, 186 (1858).

²⁴ Chalonge, D., and Zé, N. T., *J. Phys. Radium* (7), 1, 416 (1930).

²⁵ Freeman, I. M., *Astrophys. J.*, 64, 122 (1926).

²⁶ Horton, F., and Davies, A. C., *Phil. Mag.*, 46, 892 (1923).

²⁷ Lemon, H. B., *Nature*, 113, 127 (1924).

²⁸ See also Richardson, O. W., and Tanaka, T., *Proc. Roy. Soc.*, 106A, 640 (1924).

²⁹ Carst, A., *Ann. Physik*, 75, 665 (1924).

³⁰ Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, 48, 1838 (1926); see also Bates, J. R., and Taylor, H. S., *Ibid.*, 49, 2441 (1927).

³¹ Gehrcke, E., and Lau, E., *Ann. Physik*, 76, 673 (1925).

³² Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, 122, 287 (1926).

³³ Bay, Z., and Steiner, W., *Z. Physik*, 45, 337 (1927).

density high, the luminous portion of the tube was constricted. One of their tubes was water-cooled at the constriction. The tube (Figure 81) consisted of an ordinary glass tube (L) 60 centimeters long and 5 millimeters in diameter X, two electrode vessels (G), one of which has a tube (R) carrying a quartz or fluorite window and the other a 5-liter bulb (V). The apparatus was supported with the lower luminous tube in a bath with flowing water. The tube was filled with hydrogen at 1-2 millimeters pressure and sealed. Failures of these tubes led them to develop a tube that would operate under loads up to 500 or even 700 milliamperes,⁸⁴ which is important since the ultraviolet emission increases with the current density. The ratio of ultraviolet emission to the radiations in the visible range increases with the hydrogen pressure. For the continuous radiation from the hydrogen lamp, the ratio is 6:1, while that of the mercury lamp is only 0.6:1. Bay and Steiner⁸⁵ also made use of an electrodeless oscillating discharge in well-dried hydrogen.

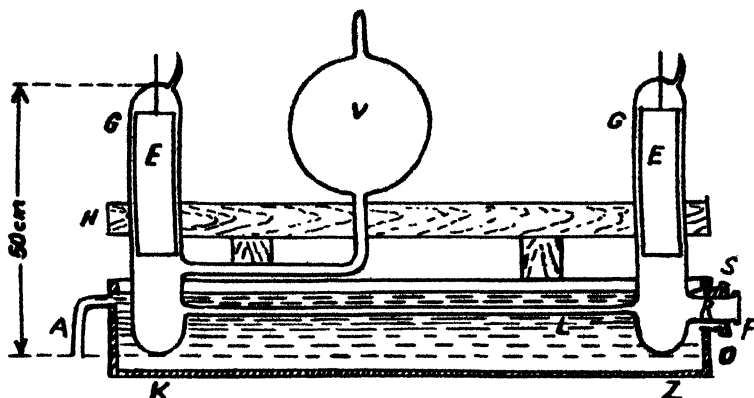


FIGURE 81. Hydrogen Discharge Tube of Bay and Steiner (*Zeitschrift für Physik*).

Another development of the discharge tube was made by Lambrey and Chalonge,⁸⁶ who used only 15-30 milliamperes to operate the tube for five minutes. They⁸⁷ extended their work to include tubes with both interior electrodes and tubes with only exterior electrodes operating at 500,000 cycles. They found that as the pressure increases, the intensity of the continuous spectrum passes through a maximum at a hydrogen pressure of 2-3 mm. For a given pressure, the intensity increases with the current, but the energy distribution is not modified. As compared with a carbon arc, the intensity is about 2.1 times as great at 4400 Å and 23 times as great at 2200 Å.⁸⁸

Considerably greater currents were carried in a tube devised by Lawrence and Edlefsen.⁸⁹ The electrodes were aluminum cylinders 6 centimeters in diameter and 40 centimeters long, open at the bottom and closed at the top, and attached to tungsten leads passing through "Pyrex" containing tubes. The bottom edges of elec-

⁸⁴ Bay, Z., and Steiner, W., *Z. Physik*, 59, 48 (1922).

⁸⁵ Bay, Z., and Steiner, W., *Z. Elektrochem.*, 34, 657 (1928).

⁸⁶ Lambrey, M., and Chalonge, D., *Compt. rend.*, 184, 1057 (1927).

⁸⁷ Lambrey, M., and Chalonge, D., *Compt. rend.*, 188, 1104 (1929).

⁸⁸ See also Chalonge, D., and Zé, N. T., *Compt. rend.*, 190, 632 (1930); Chalonge, D., *Z. Astrophys.*, 15, 82 (1938).

⁸⁹ Lawrence, E. O., and Edlefsen, N. E., *Rev. Sci. Instruments*, 1, 45 (1930).

trodes were rounded off and made close-fitting to the containing tubes for cooling by conduction. The two large "Pyrex" tubes containing the electrodes were joined through a tube of quartz 7 millimeters in diameter and 60 centimeters long. The connecting tube was sealed to the confining tubes by a water-cooled wax joint. The tube was inserted into short quartz tubes of larger diameter at each end and the larger quartz tubes were waxed to "Pyrex" side tubes. Two inflow jets of water flowed in the region between the small and large quartz tubes and kept the wax joints cool despite the great generation of heat nearby. The whole tube was immersed in a tank of water to the dotted line (Figure 82). This cooling was adequate for 6.5 amperes at 3000 volts, but the tube was ordinarily run at 3 amperes. There was some unsteadiness and bumping at the middle of the connecting tube unless additional water jets were provided along the quartz tube. The tube was used end-on, through a quartz window W waxed on a "Pyrex" side tube through the tank wall.

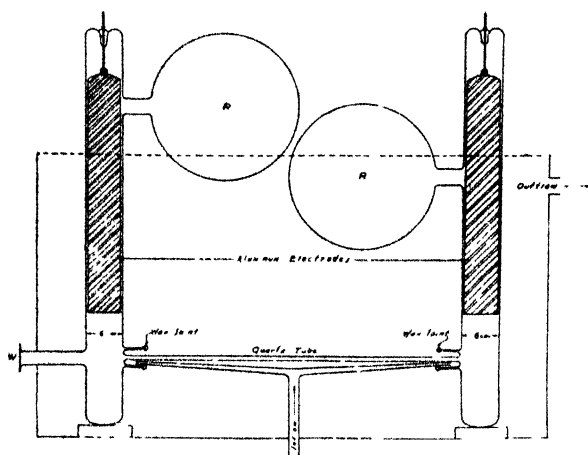


FIGURE 82. Water-cooled Hydrogen Discharge Tube of Great Carrying Capacity (Lawrence and Edlefson, *Review of Scientific Instruments*).

It was only necessary to evacuate the tube by an oil pump to 0.01 millimeter and flush it several times with commercial tank hydrogen. The pressure was not very critical, and the hydrogen pressure was merely reduced to allow a discharge of several amperes to pass at 3000 volts. Lines appeared at first but after several hours to a day of operation, the lines due to impurities disappeared and the region from 3000 to 2000Å became continuous. Two large flasks (R) served as hydrogen reservoirs. The tube could be operated steadily over long periods. Data obtained by the aid of a monochromator and thermopile indicated that the intensity of the ultraviolet does not vary greatly from the near ultraviolet to 2000Å. The intensity at 2536Å seemed of the same order as that obtained from a Cooper-Hewitt lamp at ordinary currents. The tube yielded about ten times the intensity of the first Bay and Steiner tubes, and was much more intense than the usual ultraviolet available for spectroscopy, exposures of 0.1 second being adequate.

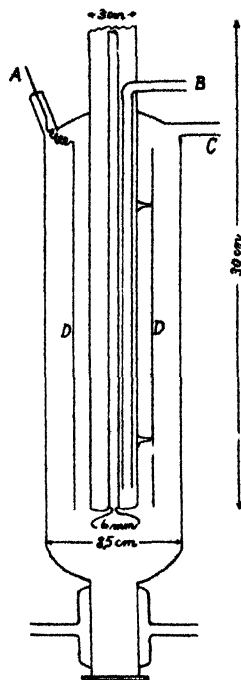
Other tubes were described by Kistiakowsky⁴⁰ and by Urey, Murphy and

⁴⁰Kistiakowsky, G. B., *Rev. Sci. Instruments*, 2, 549 (1931).

Duncan.⁴¹ The latter tube, of glass, was very compact and so well cooled that currents up to 2 amperes could be carried for long exposures without breakage. One end only is indicated in Figure 83; the other is identical. The tube was composed of "Pyrex" with crystal quartz windows stuck on each end with de Khotinsky cement. The electrodes D were cylinders of sheet aluminum, the edges of which were spot welded. They were joined to the tungsten lead A by German silver wire. The electrodes were held by glass prongs. A rapid stream of water flowed into B and after circulating around the inner tube flowed out again at the other end. Two small cooling jackets were placed near the windows to prevent the wax from getting warm, but they did not seem necessary. The inner tube through which the discharge passed was moistened with silver nitrate solution which was readily

FIGURE 83.

Hydrogen Discharge Tube of Urey, Murphy, and Duncan (*Review of Scientific Instruments*).



reduced to silver by the discharge. The tube was evacuated at C and in the same position at the other end a palladium tube was connected by a soft glass-to-"Pyrex" graded seal. Hydrogen was admitted through the palladium by heating the latter with a small hydrogen flame. The discharge was run repeatedly with the addition of hydrogen and evacuation until the spectrum seemed satisfactory, as viewed with a direct-vision spectroscope. The tube was sealed off from the pumping system at C. As the hydrogen gradually cleaned up, more could easily be added at the palladium tube. A 5-kv. autoregulating transformer supplied the high potential. With 110 volts and about 50 amperes on the primary, it gave 2500 volts on the secondary. An ammeter in series with the tube showed 2 amperes under the best operating conditions. A fan was directed on the outside of the tube as a further aid to

⁴¹ Urey, H. C., Murphy, G. M., and Duncan, J. A., *Rev. Sci. Instruments*, 3, 497 (1932)

cooling. Even after long exposures, the tube remained quite cool, and was satisfactory after a year of use. Employed with the Hilger E1 spectrograph, it was possible to obtain certain bands of nitric oxide at 2050 and 2150A in absorption with exposures of one to five minutes, using Eastman U. V. Spectroscopic Plates. Dawson⁴² described a tube for discharge in hydrogen at 30 to 100 millimeters pressure. The tube could be viewed side-on through a constricted quartz tube joining two hollow electrodes in glass supporting tubes.⁴³

According to Henry, the hydrogen discharge tube has become the most suitable and probably also the most used continuous source.⁴⁴ Most such tubes give intensities which are too weak. Henry modified somewhat the disposition of the electrodes and employed hydrogen at a pressure of 4 millimeters. He used 1200 volts at the electrodes and usually 2 amperes, although this could be raised to 3.5 to 4 amperes.

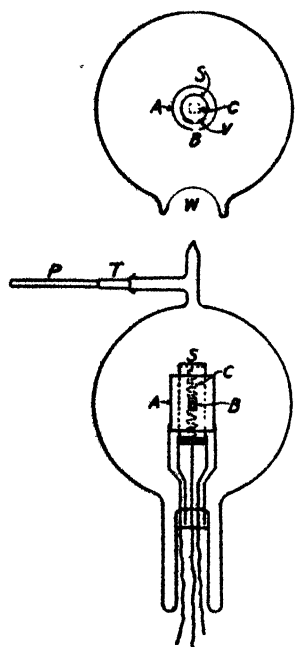


FIGURE 84.

Hydrogen Discharge Tube of Munch (*Journal American Chemical Society*).

Munch⁴⁵ states that the hydrogen continuum may be excited at about 5 per cent of the voltage required by other discharge tubes and without water cooling, by means of thermoelectrons from a hot cathode. For example, the low voltage arc of Duffendack and Manley⁴⁶ may be utilized. This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. Munch modified this tube by employing an oxide-coated cathode (C in Figure 84). This cathode is a 0.48×15.25 centimeter piece of nickel gauze bent into a corrugated form having a 0.48 centimeter cross-

⁴² Dawson, L. H., U. S. P. 1,922,281, Aug. 15, 1933; *Chem. Abs.*, 27, 5006 (1933).

⁴³ See also Stevens, D. S., *Rev. Sci. Instruments*, 6, 40 (1935).

⁴⁴ Henry, L., *J. chim. phys.*, 31, 665 (1934).

⁴⁵ Munch, R. H., *J. Am. Chem. Soc.*, 57, 1863 (1935).

⁴⁶ Duffendack, O. S., and Manley, J. H., *J. Opt. Soc. Am.*, 24, 222 (1934).

section, suspended between a cathode shield of nickel and a nickel wire and coated with barium and strontium carbonates. The cylindrical cathode shield, S, of 0.125 millimeter nickel, 4.06 centimeters long and 1.25 centimeters in diameter, forms one lead to the cathode and is closed at the bottom by means of a porcelain disk through which the second cathode lead passes. The only opening in the shield is a 0.66×3 millimeter slit cut in a piece of 0.25 millimeter sheet tungsten welded in the side. The surrounding anode (A) is a 2.2×2.86 centimeter nickel cylinder with a hole (B) to correspond to the slit in the cathode shield. The electrodes are mounted on a five-wire stem and sealed into a 10-centimeter "Pyrex" bulb. A thin window (W) is made opposite the slits by blowing a bubble about 3.2 centimeters in diameter, melting it back to about half its height and sucking it in carefully. The palladium tube (P) is silver soldered to a copper tube (T) the end of which is flared and sealed on the outside of a piece of Nonex which is fused to the "Pyrex" from which the bulb is made. The tube is evacuated and freed of all traces of moisture or carbon monoxide. The glass and metal parts are outgassed by passing a discharge through the tube and sweeping it out with a stream of hydrogen at 2-4 millimeters pressure. The hydrogen is admitted by holding a Bunsen burner under the palladium tube. When the spectrum becomes continuous below 3657Å, the tube is sealed off. The cathode requires 9 amperes at about 3 volts, supplied by a step-down transformer and connected in series with a rheostat and ammeter. The anode circuit, also containing a rheostat and ammeter, may be connected to any 110-volt circuit. In operation, the potential drop between anode and cathode is 30-35 volts. The whole discharge between the cathode and anode must pass through the small slit in the shield and is viewed through the opening in the anode. It can operate continuously at a current of 1.5 ampere, the current density being 75 amperes per square centimeter. This may be increased considerably for short periods. In comparison with the intensity of the mercury lines of a "Labarc," both sources being run at 1 ampere, the continuum was 25 per cent as intense as the 2483 and 2652Å lines, 7 per cent as intense as the 2894 and 3022Å lines and 12 per cent as intense as the 3350Å lines.

Other descriptions of tubes for this purpose were made by Watson and Hurst,⁴⁷ Almasy and Kortüm,⁴⁸ Jacoby,⁴⁹ and Smith.⁵⁰ Hydrogen discharge tubes carrying up to 1 ampere have been prepared by the Hanovia Co.

According to the Hilger Co., the distribution of radiation from hydrogen discharge tubes is so far from uniform that the tubes cannot be used for measurements of density with their "Spekker" photometer. Furthermore, when run on alternating current, the intensity of radiation increases to a maximum and dies away to zero once in each half-phase of the applied alternating current, so that it cannot be assumed that for any speed at which the use of a sector fulfills the reciprocity law, the effective density of the sector can be derived from its aperture. To overcome this, a rocking quartz tube has been made available. Its speed of oscillation is such that the energy received by the apertures of the "Spekker" photometer is uniform over that area, in a vertical plane, for all exposures over twenty seconds.

Smith and Fowler⁵¹ have described a 220-volt d.c. discharge tube which can be operated with currents as high as 20 amperes to give an intense ultraviolet continuum. (Figure 85). The cathode of 25 cm. of 40 mil tungsten wire was attached

⁴⁷ Watson, W. H., and Hurst, D. G., *Can. J. Research*, **13A**, 19 (1935).

⁴⁸ Almasy, F., and Kortüm, G., *Z. Elektrochem.*, **42**, 607 (1936).

⁴⁹ Jacoby, G., *Z. tech. Physik*, **17**, 382 (1936); *Physik. Z.* **37**, 808 (1936).

⁵⁰ Smith, N. D., *J. Opt. Soc. Am.*, **32**, 2832 (1938). This tube uses a 5.3 cm. capillary of rectangular cross-section 1.3×6 mm., with a gas pressure of 1-2 mm.

⁵¹ Smith, A. E., and Fowler, R. D., *J. Opt. Soc. Am.*, **26**, 79 (1936).

to the water-cooled cathode leads of copper tubing by set screws. The leads were attached to the "Pyrex" cathode section (C) by copper-to-"Pyrex" seals (F). The filament current (50-60 amperes) was supplied by a 220 to 30-volt transformer. The discharge tube (A) was of 7 mm. inside diameter quartz tubing attached to a 100 cc. quartz flask, which was sealed with picein to a water-cooled metal ring (B). This metal ring in turn was sealed with picein to the cathode section (C). The anode consisted of a hollow copper male joint (D), sealed with picein to a No. 50 Pyrex joint (E), the anode chamber. The latter was attached to the quartz discharge tube by means of a water-cooled picein seal. A quartz window was sealed to

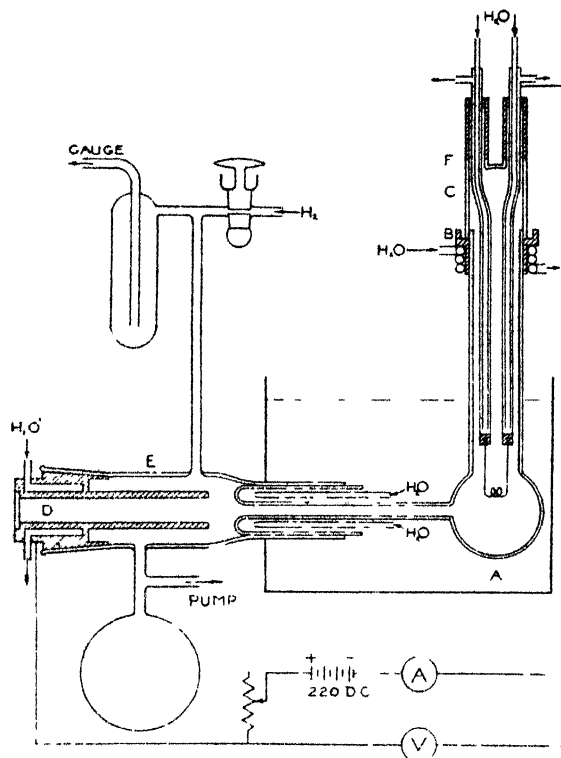


FIGURE 85. Hydrogen Discharge Tube of Smith and Fowler (*Journal Optical Society of America*).

the far end of the hollow anode. For a given potential across the tube, the pressure for greatest intensity of the continuum was not very critical, but it varied greatly with the voltage. Pressures of 0.20 to 0.27 mm. were usually employed with potentials of 220 volts.

THEORY OF THE CONTINUOUS SPECTRA OF HYDROGEN

To discuss the many investigations directed toward an understanding of the theory of the origin of the continuous spectrum which extends from the visible to the Schumann region would lead us far beyond the scope of this book. A thorough discussion of the origin of the continuous spectra of gases, with 323 references, has

been given by Finkelburg.⁵² Chalonge and Zé⁵³ have reviewed in detail the work relating to the hydrogen spectrum. Beyond the Balmer lines there lies (as discussed in Chapter 2) a continuous spectrum related to the excitation of the hydrogen atom beyond its ionization potential, as explained by Bohr.⁵⁴ In the discharge tube, the Balmer lines are widened by the Stark effect and the related continuous spectrum is displaced toward the red. Chalonge and Zé⁵⁵ have found evidence also for the existence of another continuous spectrum similarly related to the Paschen series of lines and extending into the infrared.

These continuous spectra are not, however, very significant in the radiations emitted by the tubes described in the preceding section. The effective continuous spectrum is related to the hydrogen molecule, which itself produces a "secondary," many-lined, or band, spectrum, regarding which there is a vast literature. One of the earliest theories relating the hydrogen molecule to the continuous spectrum produced in these sources assumed the spectrum to be due to dissociation of the hydrogen molecules into atoms possessing various kinetic energies, the radiations being emitted during their recombination.⁵⁶

Discrepancies in regard to the relation between the heat of dissociation of the hydrogen molecule and the long wave-length limit of the continuum led to a number of suggestions in which variously excited, rather than resting state, molecules were regarded as dissociating.⁵⁷

More recently, efforts have been directed toward the examination of the potential energy curves for the atoms of the hydrogen molecule from the standpoint of the wave-mechanics, the general features of which in relation to photochemistry are discussed in Chapter 13. For the reader desiring to study the application of these theoretical developments to the hydrogen continuum a few significant papers are cited.⁵⁸

⁵² Finkelburg, W., *Physik. Z.*, **31**, 1 (1930).

⁵³ Chalonge, D., and Zé, N. T., *J. Phys. Radium*, (7) **1**, 416 (1930).

⁵⁴ Bohr, N., *Phil. Mag.*, **26**, 17 (1913).

⁵⁵ Chalonge, D., and Zé, N. T., *Compt. rend.*, **189**, 243 (1929); **190**, 425 (1930).

⁵⁶ Schüler, H., and Wolf, K. L., *Z. Physik*, **33**, 42 (1925).

⁵⁷ Takahashi, Y., *Japan. J. Phys.*, **4**, 103 (1927); *Chem. Abs.*, **21**, 3829 (1927). Takahashi, Y. and Fukumoto, Y., *Sci. Repts. Tohoku Imp. Univ.*, **17**, 675, 963 (1928); *Chem. Abs.*, **23**, 3834 (1929). Freeman, I., *Astrophys. J.*, **64**, 122 (1926). Oldenberg, O., *Z. Physik*, **41**, 1 (1927). Herzberg, G., *Physik. Z.*, **28**, 727 (1927). Jezewski, H., *Compt. rend. soc. polonaise phys.*, **3**, 161 (1927); *Chem. Abs.*, **23**, 5106 (1929). Newman, *Phil. Mag.*, **6**, 807 (1928). Kaplan, J., *Proc. Nat. Acad. Sci.*, **13**, 760 (1927). Winans, J. G., and Stueckelberg, E. C. G., *Ibid.*, **14**, 867 (1928); Franck, J., and Jordan, P., "Anregung von Quantensprungen durch Stöße," p. 261, Berlin, J. Springer, 1927.

⁵⁸ Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927). Sugiura, Y., *Z. Physik*, **45**, 484 (1927); *J. Phys. Radium*, **8**, 113 (1927). Birge, P., *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Condon, E. U., *Phys. Rev.*, **28**, 1182 (1926); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Franck, J., *Trans. Faraday Soc.*, **21**, part 3, (1925). Epstein, P. S., and Muskat, M., *Proc. Nat. Acad. Sci.*, **15**, 405 (1929). Goldstein, L., *Compt. rend.*, **193**, 485 (1931). Smith, A. E. and Fowler, R. D., *J. Opt. Soc. Am.*, **26**, 79 (1936); McDonald, J. K. L., *Proc. Roy. Soc.*, **A 136**, 528 (1932). Finkelburg, W., and Weizel, W., *Z. Physik*, **68**, 577 (1931).

Chapter 10

Protective Glasses, Ultraviolet-Transmitting Glasses and Filters

The ability of glasses of various compositions to absorb or transmit ultraviolet or other radiations is of importance when viewed from either of two opposite aspects. It may be desired on the one hand to develop a glass capable of protecting the eyes of a worker from injurious radiations, or, on the other, it may be desired to produce a glass which transmits the solar ultraviolet more completely than ordinary window glass.¹ Mention of protective glasses is made here to remind the experimentalist not to disregard suitable protection for the eyes when working with ultraviolet rays.

PROTECTIVE GLASSES

Exposure to rays emitted in electric welding and in the employment of the oxy-acetylene torch for cutting and welding steel has been the cause of many cases of inflammation of the eyes. In arc welding, the eyes require protection from intense visible light or glare, from intense infrared or heat rays and from ultraviolet radiations. Andrews² affirms that the ultraviolet rays are the most dangerous because they are not only invisible but also because we are unprovided by nature with any organ or sense for detecting them. Furthermore, it should be noted that the harmful effects are not immediately produced but become evident only some time after the exposure. Fortunately, the most deleterious of the ultraviolet rays are absorbed by a moderate thickness of ordinary glass.

The symptoms of conjunctivitis caused by intense light or by ultraviolet rays are abnormal intolerance to light, excessive secretion of tears, intense smarting of the lids, contraction of the pupils, sometimes swelling of the lids, and more rarely, small ulcers developing on the eyeball or cornea. Fortunately, the lesions are usually superficial, because the cornea absorbs all radiations below 3000A and the lens those below 3500A, thereby protecting the retina. However, unless properly treated by a physician, infection may occur, resulting in chronic inflammation of the conjunctiva, cornea, iris or retina and possibly blindness. Under proper treatment, most cases recover in a few days.

In 1914, Crookes³ investigated over 300 specimens of glass in an endeavor to find a colorless glass which would absorb all the ultraviolet and infrared rays. Although he did not find a colorless glass which met this specification, he developed a blue-green glass which absorbed about 90 per cent of the radiant heat and which was opaque to ultraviolet rays. The glass was sufficiently free from color to be scarcely noticeable when used as spectacles. The ideal glass which will transmit all

¹Chance, W. H. S., and Hampton, W. M., [*Proc. Optical Convention*, 1926, 1, 24; *Chem. Abs.*, 21, 3111 (1927)], reviewed the early manufacture of the filtering glasses produced by Chance Bros. & Co., Ltd. Methods of measuring the transmission of ultraviolet rays by glasses were discussed by Shapiro, C. V., *Am. J. Physiol.*, 87, 396 (1928), and Schachtschabel, K., *Ann. Physik*, 81, 929 (1926).

²Andrews, W. S., *Gen. Electric Rev.*, 9, 303 (1917).

³Crookes, W., *Trans. Roy. Soc.*, 214, 1 (1914).

the colors of the spectrum, cutting off the invisible rays at each end, has still to be discovered.

Luckiesh,⁴ Gage⁵ and Martin⁶ have given data on the transmission of the earlier commercial protective glasses. The latter also have been studied at the Bureau of Standards.⁷

A number of commercial glasses, including 82 examined by Gibson and McNicholas, were investigated. Crookes A, Corning 91B, American Optical Co. Nos. 57 and 58, and Noviol O were most efficient in protecting against ultraviolet rays. The latter two, the most efficient, were not nearly so colorless as the other three. A combination of Noviol A and Corning 124J absorbs all the ultraviolet and most of the infrared and, although light green, still has a high visible transmission.⁸ The Bureau developed a blue glass for furnace workers by replacing half the lime in a soft soda-lime glass with cerium oxide to stop the ultraviolet and adding sufficient cobalt oxide to produce the blue color desired by workmen. The glass registered 20 + 8 on the Lovibond scale.⁹ The glass may contain SiO₂ 60-80, CaO 0-12, CeO 5-10, CoO 0.1-0.5 and Na₂O 12-25 percent.¹⁰ A thin film of gold¹¹ absorbs infrared and ultraviolet and to some extent visible rays, depending upon the density of the film.¹² Inagaki reported Noviweld and certain Crookes glasses suitable for specified uses in glass plants.¹³ Coblenz and Stair¹⁴ have published transmission curves of optical crown glass, and several commercial protective glasses. See Figure 86.^{14a} Average samples of colorless, vitreous silica were much more opaque than was quartz to radiation shorter than 2400Å. A formula for specifying the shade number of protective glasses, based upon experimental tests, was given, together with a table of transmissions and tolerances, corresponding to shade numbers, as proposed by a Federal specification committee. The specifications were somewhat revised in 1930.¹⁵

A glass advocated by the Corning Glass Works¹⁶ for absorbing ultraviolet radiations is made by adding to an ordinary lime, barium, lead, or zinc glass batch; (A) at least 6 per cent of titanium dioxide, and oxidizing salt (nitre) in sufficient quantity to prevent the reduction of the titanium dioxide, with or without cerium oxide or vanadium oxide; or (B) at least 1 per cent of an oxide of vanadium higher

⁴ Luckiesh, M., *Trans. Ill. Eng. Soc.*, **9**, 472 (1914).

⁵ Gage, H. P., *Ibid.*, **11**, 1050 (1916); **25**, 337 (1930).

⁶ Martin, L. C., *Trans. Opt. Soc.*, **18**, April (1917).

⁷ Coblenz, W. W., and Emerson, W. B., *Tech. Paper No. 93* (1917), *Bureau of Standards, J. Frank. Inst.*, **183**, 629 (1917); Coblenz, W. W., Emerson, W. B., and Long, M. B., *Bull. Bureau of Standards*, **14**, 663 (1918); *J. Frank. Inst.*, **188**, 255 (1919); Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech. Paper No. 119* (1919); *J. Frank. Inst.*, **187**, 630 (1919). For data on the absorption of cobalt glasses, see Brode, W., *J. Am. Chem. Soc.*, **55**, 939 (1933).

⁸ See also Wright, P., *Brit. J. Radiology*, **2**, 434 (1929).

⁹ *Ind. Eng. Chem., News Ed.*, **3**, No. 24, 6 (1925); Coblenz, W. W., U. S. P. 1,637,439, Aug. 2, 1927; *Chem. Abs.*, **21**, 3114 (1927).

¹⁰ Coblenz, W. W., and Finn, A., *J. Am. Ceram. Soc.*, **9**, 423 (1926); *Brit. Chem. Abs.*, **B**, 667 (1926).

¹¹ Finely divided gold particles have also been proposed; Warde, F. M. *British P.* 341,187, Nov. 15, 1929; *Chem. Abs.*, **27**, 2272 (1933).

¹² See Grondall, L. O., *Science*, **70**, 179 (1929). For other metallic films obtained by cathodic sputtering, see Taylor, E. M., Stafford, G., and Rodwell, R. V., and Kapella, Ltd., *British P.* 479,238, Feb. 2, 1938; *Chem. Abs.*, **32**, 4938 (1938).

¹³ Inagaki, T., *Rept. Lab. Asahi Glass Co.*, 1921; *Chem. Abs.*, **16**, 3185 (1922).

¹⁴ Coblenz, W. W., and Stair, R., *U. S. Bureau Standards Tech. Paper No. 369*, 555 (1928).

^{14a} The transmissions of several miscellaneous materials, as mother-of-pearl, sextant and signal glasses, heat-transmitting glass, greenish-brown glass, and the organic materials "pollopos" and "protectoid" were also given.

¹⁵ Coblenz, W. W., and Stair, R., *J. Opt. Soc. Am.*, **20**, 624 (1930).

¹⁶ *British P.* 118,397 and 118,398, April 15, 1918, to Corning Glass Works; *J. Soc. Chem. Ind.*, 584A, 1918. For snow glasses, see also Degea, A.-G., *British P.* 466,262, May 25, 1937; *Chem. Abs.*, **31**, 8144 (1937).

than V_2O_5 , with or without an oxidizing agent and a complementary, but absorptively inert substance (manganese dioxide, cobalt, nickel or uranium oxide) to change the hue of the glass from green to amber. Titanium dioxide is about half as effective as cerium oxide. A lime-soda glass containing 7.7 per cent titanium dioxide and 7.7 per cent cerium nitrate is a brilliant clear yellow, and in plates two mm. thick completely cuts off the 3650A line. A glass containing both cerium nitrate and titanium dioxide has a more brilliant color and greater desirable absorption than a glass containing one of these substances superimposed on a glass containing the other. The addition of borax increases the refractive index of the glasses containing titanium dioxide. A large percentage of borax in a glass containing

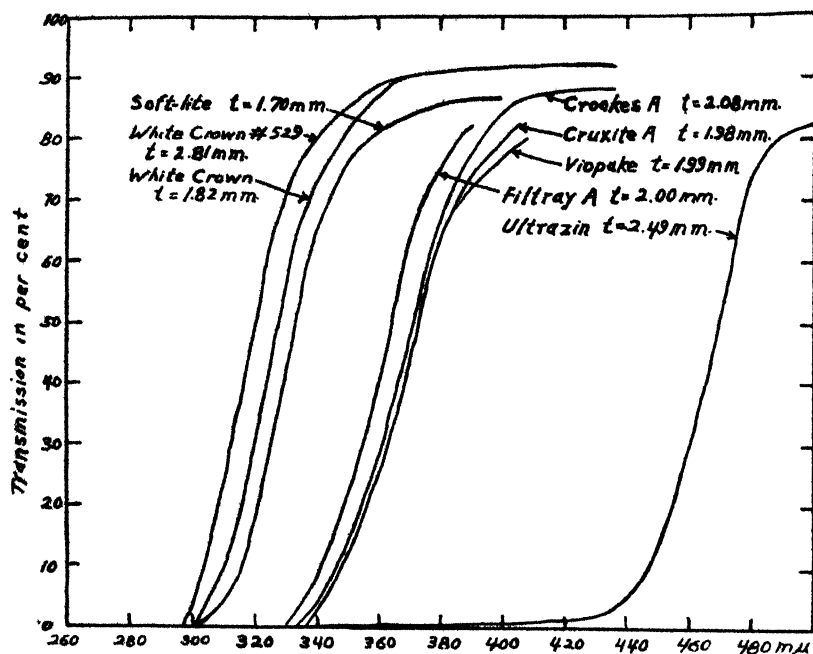


FIGURE 86. Transmission Curves for Various Protective Glasses (Coblentz and Stair, "Bureau of Standards Technical Papers").

vanadium oxide completely cuts off the ultraviolet 3650A line in plates of 4 mm. thickness. If 2 per cent of vanadium oxide be used, the same cut-off is effected by plates 2 mm. thick.

Up to 10 per cent of rare earths is used by Deutsche Spiegelglas A.-G.¹⁷ Taylor¹⁸ describes a glass for absorbing ultraviolet rays in which titanium oxide is an essential constituent. He also¹⁹ obtains a flesh-colored glass of high ultraviolet absorption and good visible transmission by using 3 to 6 per cent cerium dioxide and 0.2 per cent manganese dioxide with silica, potash, soda and lime. In another instance it was proposed to use as the only coloring oxide, 0.2 to 1 per cent

¹⁷ French P. 720,075, July 16, 1931, to Deutsche Spiegelglas, A.-G.; *Chem. Abs.*, 26, 3892 (1932).

¹⁸ Taylor, W. C., U. S. P. 1,292,147 and 1,292,148, Jan. 21, 1919; *Chem. Abs.*, 13, 1005 (1919).

¹⁹ Taylor, W. C., U. S. P. 1,414,715, May 2, 1922; *Chem. Abs.*, 16, 2206 (1922).

of ferric oxide, in making a glass which transmits no ultraviolet, but 84 per cent of the visible, through 2 mm.²⁰ To absorb both infrared and ultraviolet, not less than 0.3 per cent of cobalt and iron oxides, or 0.5 per cent of As_2O_3 and Sb_2O_3 may be added.²¹ Cadmium sulfide and ferrous oxide have also been advocated.²² A glass, said to be efficient in absorbing ultraviolet rays and practically colorless, is made by Chance Bros.²³ by using two or more ultraviolet-absorbing ingredients, the colors of which neutralize each other. A glass containing approximately 3.3 per cent of cerium and 0.7 per cent of didymium (added as oxides or hydroxides) is said to be practically colorless and efficient in absorbing ultraviolet rays. Another glass transmitting 80 per cent of visible light with but little selective absorption and cutting off all waves shorter than 3800A. contains a small proportion of chromium and vanadium.²⁴ E. A. Busch A.-G. Optische Ind.²⁵ colored lenses, regulating the tint as desired, by a suitable glaze, which might be applied only to the upper edge of the glasses, through which it was stated the dangerous rays usually enter the eye. The firm of Zeiss²⁶ described a glass which greatly weakens rays between 7000 and 15,000A and those below 3600A, while transmitting the visible range. Frank²⁷ adds to the glass batch a small quantity (0.00256 part by weight) of a mixture of MnO_2 , 3 and Fe_2O_3 , 2 parts. A thickness of 1.5 mm. absorbs a large proportion of ultraviolet and infrared rays without appreciably reducing the visible. Also, it is stated that laminated glass, with intervening sheets of celluloid or the like, may be made to exclude ultraviolet.²⁸

A simple means of evaluating eye-protective glasses was proposed by Bloch.²⁹ In the ultraviolet (isolated by a "black glass" filter of the Sendlinger Optischer Glaswerke), the transmission of a standard quartz lamp light is estimated from the degree of fluorescence excited on a standard test paper. The results agree well with spectrographic determinations.

Starkie and Turner³⁰ in transmission studies of sections cut from commercial food containers and ground to 2 mm. thickness, demonstrated a rather definite increase in absorption with rise of the content of ferric oxide. Titanium dioxide also absorbs ultraviolet light, but the amounts found in commercial glasses, usually below 0.02 per cent are too small to function greatly.³¹ Translucent sheets of cellulose hydrate are rendered impermeable to ultraviolet rays by treatment with aqueous pine bark extract, according to Gerngross and Callo.³²

²⁰ French P. 760,998, March 7, 1934, to Pittsburgh Plate Glass Co.; *Chem. Abs.*, 28, 4195 (1934).

²¹ German P. 550,782, May 6, 1927, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, 26, 4929 (1932).

²² French P. 752,615, Sept. 27, 1933, to Veeries de Goetzenbruck; *Chem. Abs.*, 28, 1160 (1934).

²³ Gell, P. V. W., Gould, C. E., Hampton, W. M., and Martin, H. S., U. S. P. 1,634,182, June 28, 1926, to Chance Bros. & Co., Ltd.; British P. 256,737, June 5, 1925; *Brit. Chem. Abs.*, B, 878 (1926); *Chem. Abs.*, 21, 2775 (1927).

²⁴ Gould, C. E., British P. 316,464, Sept. 8, 1928, to Chance Bros. & Co., Ltd.; *Brit. Chem. Abs.*, B, 816 (1929).

²⁵ German P. 424,811, Jan. 10, 1925, to E. A. Busch, A.-G. Optische Ind.; *Brit. Chem. Abs.*, B, 789 (1926).

²⁶ British P. 252,130, May 16, 1925, to Firm of C. Zeiss Co.; *Chem. Abs.*, 21, 1528 (1927).

²⁷ Frank, I., U. S. P. 1,615,448, Jan. 25, 1927; *Brit. Chem. Abs.*, B, 365 (1927); *Chem. Abs.*, 21, 808 (1927).

²⁸ Murray, G. H., U. S. P. 1,958,013, May 8, 1934; *Chem. Abs.*, 28, 4196 (1934).

²⁹ Bloch, L., *Gas und Wasserfach.*, 70, 1229 (1927); *Chem. Abs.*, 22, 850 (1928); *Brit. Chem. Abs.*, B, 231 (1928). See also Danckwortt, P., and Jürgens, E., *Arch. Pharm.*, 772, 713 (1934).

³⁰ Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, 12, 27 (1928); *Chem. Abs.*, 22, 2821 (1928).

³¹ Smith, A. W., and Sheard, C., [*J. Opt. Soc. Am.*, 2, 26 (1919)] gave earlier work on the absorption of ultraviolet light by glasses.

³² Gerngross, O., and Callo, A., U. S. P. 2,106,599, Jan. 25, 1938; *Chem. Abs.*, 32, 2654 (1938).

GLASSES PERMEABLE TO ULTRAVIOLET RADIATIONS

After the discovery of the antirachitic properties of the ultraviolet rays of sunlight (Chapter 38), glass manufacturers sought to develop glasses capable of transmitting all the health-giving solar rays which reach the earth. For use in optical instruments, ultraviolet transmitting glasses had been, however, produced much earlier (about 1907) and Schott and Co. early marketed Uviol glasses, which were, unfortunately, expensive and unstable.³³ According to the historical summary by Davidovitch,³⁴ Eder and Valenta³⁵ pointed out that phosphate crown glass has a considerable transparency in the ultraviolet. Zschimmer³⁶ found that barium oxide had similar properties, but that glasses should be free from alkali metal oxides to increase ultraviolet transparency.³⁷ Sodium oxide glass is less transparent than that with potassium oxide. Glass with lead oxide is especially poor. Fritsch³⁸ found a generous proportion of B_2O_3 to confer excellent transparency. A glass of 6 parts of calcium fluoride and 14 of B_2O_3 was said to be transparent down to 1850Å. Such glasses have been employed in spectrographic optical systems. Lithium glasses are said to be very transparent to short wave-lengths, but are unstable. While developing certain blue glasses, Luckiesh³⁹ noticed that cobalt glass appeared to be more transparent than clear glass in the region of 3000Å.

Sugie⁴⁰ after investigation of the ultraviolet absorption of over fifty samples of soda-lime glasses, found no systematic relation between the absorption and the composition of the glass. Substituting sodium by potassium did not alter the transmission. Phosphorus pentoxide had no effect, but Sb_2O_3 , TiO_2 , Fe_2O_3 , MgO and Al_2O_3 decreased the penetration. His most transparent glass had the composition: Na_2O , 1, CaO , 1.4 and SiO_2 , 6 parts; this transmitted through 1.5 mm. wave-lengths as short as 2370Å. The least transparent of his series had 1.5 parts of CaO and transmitted down to 2790Å. It must be noted, however, that the shortest wave-length which gets through is not as significant a criterion of the quality of a glass as are the fractions of the incident radiation of various wave-lengths which are transmitted. This is true because the drop in the transmission curve is usually not sharp, but extends over several hundred Ångström units in many cases. Sugie found also that up to a certain point, nickel makes glass more transparent to the ultraviolet. When potash rather than soda is present, a nickel glass is black, although it transmits in the ultraviolet. Cobalt can be substituted for nickel in such glasses, but the use of both cobalt and nickel in the same glass diminishes the ultraviolet transmission. In soda-lime (but not potash-lime) glasses, ferric iron lowered the penetrability more than did ferrous iron. Chromium in small quantities had little effect. The effect of manganese is slight up to, but great above, 1 per cent.⁴¹ Locke used a high proportion of alumina and avoided alkalies. In general, perme-

³³ Rüttenauer, A., *Sprechsaal*, 61, 449,453 (1928); *Chem. Abs.*, 23, 2543 (1929).

³⁴ Davidovitch, P., *J. Opt. Soc. Am.*, 20, 627 (1930).

³⁵ Eder, J. M., and Valenta, E., *Denkschriften, Wiener Akad. Wissenschaften Math. Nat. Kl.*, 61 (1894).

³⁶ Zschimmer, E., *Z. Instrumentkunde*, 23, 360 (1903).

³⁷ Zschimmer, E., *Physik. Z.*, 8, 611 (1907).

³⁸ Fritsch, C., *Physikal. Z.*, 8, 518 (1907).

³⁹ Luckiesh, M., *J. Frank. Inst.*, 186, 111 (1918).

⁴⁰ Sugie, S., *Rept. Osaka Ind. Research Lab.*, 5, No. 11, 1-26 (1924); No. 15, 1-19; 6, No. 4, 1-26; *Chem. Abs.*, 20, 3218 (1926).

⁴¹ For further chemical data, see Locke, F. M., *Glass Ind.*, 7, 136 (1926); *Chem. Abs.*, 21, 3435 (1927); Weidert, F., *Sprechsaal*, 64, 992 (1932); Jaeckel, G., *Z. tech. Physik*, 7, 301 (1926); *Chem. Abs.*, 20, 3066 (1926); Gilard, P., Swings, P., and Hautot, A., *Rev. belg. ind. verrieres*, 2, 2, 26, 50, 74, 98 (1931); *Bull. sci. Acad. Roy. Belg.*, 17, 235, 362 (1931); 15, 749 (1929); *J. Soc. Glass Tech.*, 15, 488; *Chem. Abs.*, 26, 6086 (1932); Fromberg, B. M., and Oshchepkov, F. P., *Russian P.* 44,317, Sept. 30, 1935; *Chem. Abs.*, 32, 3112 (1938).

ability increases with the silica content. Barium oxide is superior to lime which, in turn, is better than zinc oxide.

One of the more important lines of development which made possible the commercial production of ultraviolet glasses has been the reduction of those impurities in the raw materials, notably ferric and titanium oxides, which are recognized as increasing the ultraviolet absorption of ordinary silicon-lime-alkali glasses. Hadden⁴² produced a glass (4 mm. plates of which are transparent to light waves shorter than 3000Å) by reducing the iron impurities to less than 0.055 per cent (as ferric oxide) and the titanium oxide to less than 0.050 per cent. The melting was carried out in a crucible free from these oxides, under non-oxidizing conditions, *e.g.* in the presence of carbon, chromium, uranium, vanadium or nickel. The glass (980Å) has a density 2.64 and a refractive index 1.539. The cost of production was above that of window glass, but far below that of quartz.⁴³ The Corning Co. makes a series of such Corex glasses. According to Gibson of the Bureau of Standards⁴⁴ 2 mm. sheets transmit 86 per cent of the radiations at 2900Å. This figure is uncorrected for reflection losses of approximately 8 per cent. Corex is available either polished or unpolished, the latter having the same ultraviolet transmission, but not affording clear vision. A change of thickness does not greatly alter the transmission in the biologically important range between 2900 and 3100Å.⁴⁵ The deleterious effect of ferric oxide was also recognized by Fuwa and Hiraoka,⁴⁶ who found the shortest wave-length transmitted by 4.30 mm. of a plate glass containing 0.090 per cent of the oxide to be 3021Å. Only 3065Å was transmitted by a much thinner plate, 2.78 mm., of a window glass containing 0.103 per cent iron oxide. Starkie and Turner⁴⁷ concluded from an extrapolation of their results on the transmission of glasses containing from 0.005 to 1 per cent of iron oxide, that the limiting transmission of a glass free from iron oxide would be 2230Å.⁴⁸ Klumb and Hasse⁴⁹ proposed the use of very thin (10 μ) glass windows for scientific work in the ultraviolet region.

By 1926, there had appeared on the market "Vitaglass," probably the first ultraviolet-transmitting glass manufactured in panes on a large scale.⁵⁰ The glass was developed by Lamplough, of Trinity College, Cambridge,⁵¹ and was claimed to transmit about 40 per cent of all incident energy in the region 3130 to 2900Å. Commercial production began in 1924 in the works of Chance Bros. & Co. and was later

⁴² Hadden, R., *British P.* 263,410, July 1, 1926; 298,908, Oct. 5, 1927; 319,337, Sept. 27, 1928, to Corning Glass Works; *Chem. Abs.*, 22, 148 (1928).

⁴³ Hood, H. P., *Science*, 64, 281 (1926); *Chem. Abs.*, 20, 3788 (1926); U. S. P. 1,830,902-4, Nov. 10, 1931. The yellow color may be eliminated by including a compound of zinc. The percentage of silica and B₂O₃ should be 10 to 22 times the total percentage of alkalis and the ratio of SiO₂ to B₂O₃ greater than 5. [*German P.* 637,438, Oct. 28, 1936]

⁴⁴ Gibson, K. S., *J. Opt. Soc. Am.*, 13, 279 (1926).

⁴⁵ One way of purifying the raw materials might be to obtain the silica by precipitation from industrial solutions of soluble glass, washing it free from the impurities with sulfuric acid containing hydrogen peroxide. "Osa" participations industrielles, *French P.* 760,329, Feb. 20, 1934; *Chem. Abs.*, 28, 3549 (1934). For use of other reagents, see Dusing, W., and Enss, J., *German P.* 593,687, March 1, 1934; *Chem. Abs.*, 28, 3549 (1934); Enss, J., and Huniger, M., U. S. P. 2,107,935, Feb. 8, 1938, to General Elec. Co.; *Chem. Abs.*, 32, 2703 (1938).

⁴⁶ Fuwa, K., and Hiraoka, T., *J. Japan. Ceram. Assoc.*, 34, 504 (1926); *Chem. Abs.*, 22, 487 (1928).

⁴⁷ Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, 12, 324 (1928); *Chem. Abs.*, 23, 3550 (1929); see also *J. Soc. Glass Tech.*, 15, 365 (1931); *Chem. Abs.*, 26, 3635 (1932).

⁴⁸ A number of general review articles covering in more detail the manufacture of special ultraviolet transmitting and absorbing glasses are available: English, S., *Brit. J. Radiol.*, 4, 724 (1931); Wolf, J., *Ceram. et Verrerie*, 381 (1931); Hoffmann, J., *Sprechsaal*, 65, 591 (1932); le Braz, J., *Glaces et Verres*, 5, No. 27, 12 (1932); Grant, J., *Glass*, 9, 391 (1932); Salmony-Karsten, A., *Chem. Ztg.*, 52, 269 (1928); *J. Chem. Ind.*, 47, 36,936 (1928).

⁴⁹ Klumb, H., and Hasse, T., *Z. Physik*, 76, 322 (1932).

⁵⁰ *Chem. Age* (London), June 19, 545 (1926).

⁵¹ Lamplough, F. E., *Pottery Gazette*, 54, 1120 (1929).

extended to the works of Pilkington Bros., Ltd. The absorption by thin glass is shown in Figure 87. Tisdall and Brown⁵² found "Vitaglass" to transmit approximately one-fourth of the antirachitic rays of December sunlight.

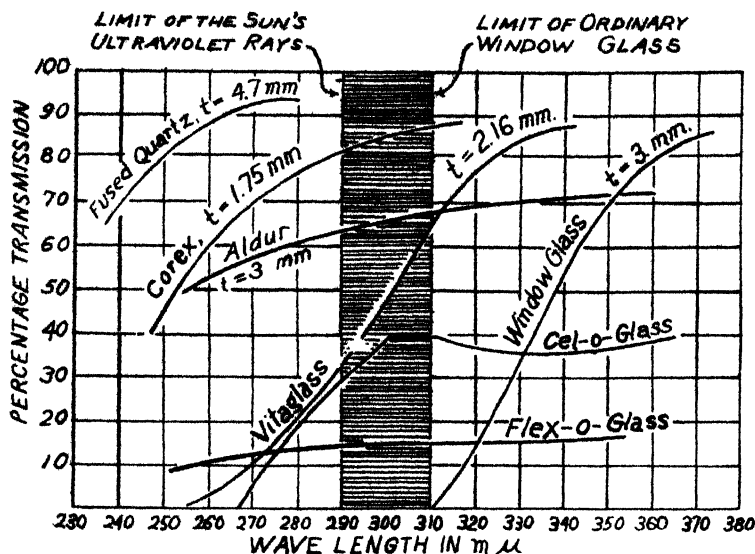


FIGURE 87. Transmission Curves for Vitaglass and Aldur (R. H. Crist, *Industrial and Engineering Chemistry*).

It must be remembered in connection with the use of ultraviolet-transmitting glasses that their effectiveness in the prevention of rickets is limited by the intensity of the incident radiation. If seasonal and atmospheric conditions, or dirt upon the glass, preclude the incidence of more than small quantities of energy in the desired wave-length band upon the glass surface, it is obvious that helpful results cannot be expected from its use. Dust and dirt may reduce the transmission at 3020Å by 30 to 40 per cent. There is comparatively little of the valuable ultraviolet in the sunlight of Chicago during the winter months.⁵³ Clark⁵⁴ estimated that a person would receive as much ultraviolet radiation in two minutes in direct sunlight at noon, as in an entire day at 5 meters behind a window of ultraviolet-transmitting glass exposed to the north sky, because the amount of ultraviolet which can enter an ordinary-sized window represents such a small part of that which is available from the entire sky.⁵⁵

Others have attempted to make ultraviolet-transmitting glasses by increasing the silica content of an ordinary glass, *e.g.*, the Quartzlite. Lai and Silverman⁵⁶ found the ultraviolet transmission of certain beryllium glasses to be greater than that of ordinary glass, but less than that of magnesium glass. Transmission decreases with

⁵² Tisdall, F. F., and Brown, A., *Proc. Soc. Exptl. Biol. Med.*, 24, 449 (1927).

⁵³ Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, 89, 187 (1928).

⁵⁴ Clark, J., *Science*, 68, 165 (1928).

⁵⁵ See also Eisenberg, K. B., *Gesundheit Ing.*, 51, 465 (1928); *Chem. Abs.*, 22, 3477 (1928); Long, B., *Science Ind.*, 12, 13 (1928).

⁵⁶ Lai, C., and Silverman, A., *J. Am. Ceram. Soc.*, 11, 535 (1928); *Brit. Chem. Abs.*, B, 895 (1928); *Chem. Abs.*, 22, 3271 (1928).

increasing beryllia content. Gould, Hampton and Martin⁵⁷ suggested the use of a batch giving a finished glass substantially free from dissolved gaseous oxides. The batch may comprise silica, borax and a powdered metal such as zinc, aluminum or tin which combines readily with oxygen and acts as a reducing agent.

English⁵⁸ gave a description of the experimental glasses which led to the development of Holviglass. Not only was the effect of iron considered, but it was stated that the admixture of either soda, potash or boric oxide with silica seriously reduces transmission by the latter. The best results were obtained with a soda-boron-silica glass, no relation between silica content and transparency being found. Alkali added as carbonate proved better than when added as the sulfate or nitrate.

Other manufacturers were concerned with the valence state of the iron oxide in the glass. Phelps⁵⁹ converted nearly all the iron in the glass to the ferric form by melting the glass under oxidizing conditions or by introducing a nitrate. This is at variance with the conclusions of many others, as Turner⁶⁰ who found for glasses containing 0.1 per cent of iron oxide a difference in transmission limits of about 100A between glasses containing the oxide in the ferrous and ferric states, the ferrous transmitting the better. Rose⁶¹ found triavalent iron to cause the absorption of 100 times more ultraviolet than ferrous iron, the limits of transmission being at 3200 and 2200A, respectively.

Various reducing agents have been employed, as charcoal, which tends to make a muddy glass, zinc chloride⁶² which makes the glass hazy, stannous oxide⁶³ or organic compounds such as urea.⁶⁴ Aluminum or magnesium powders have been proposed.⁶⁵ The addition of manganese oxide has been suggested on the ground that it undergoes oxidation in preference to the iron. Jaeckel⁶⁶ describes a glass of high transparency to ultraviolet rays containing at least 10 per cent BaO and not more than 10 per cent of B₂O₃ and not more than 3.5 moles of acid per mole of base. The glass contains no arsenous oxide and practically no ferric oxide. The N.V. Philips' Gloeilampenfabrieken⁶⁷ describes a glass substantially free from alkali oxide, consisting of at least 60 per cent of silica together with B₂O₃ and Al₂O₃. The glass softens above 600°. One proposed composition is SiO₂ 77.2, Al₂O₃ 10.7, CaO 5.4 and B₂O₃ 7.0 per cent. Smelt⁶⁸ however, uses SiO₂ 65, B₂O₃ 2, Na₂O 5.5, K₂O 9.5, BaO 15 and ZnO about 3 per cent; iron (in traces) and a fluoride about 1 per cent were incorporated in the mixture.

Beryllium fluoride glasses have been said to transmit to 2200A⁶⁹ and Ziegler

⁵⁷ Gould, C. E., Hampton, W. M., and Martin, H. S., British P. 312,728, March 19, 1928; *Chem. Abs.*, 24, 937 (1930).

⁵⁸ English, S., *Glass*, 5, 338 (1928); 8, 52 (1931); *Chem. Abs.*, 23, 252 (1929).

⁵⁹ Phelps, D. V., British P. 320,904, July 25, 1928, to Pilkington Bros.; *Chem. Abs.*, 24, 2566 (1930).

⁶⁰ Turner, W. E. S., *J. Soc. Chem. Ind.*, 48, 65T (1929); *Chem. Abs.*, 23, 3063 (1929); *Brit. Chem. Abs.*, B, 355 (1929); see also Andresen-Kraft, C., *Glastech. Ber.*, 9, 577 (1931).

⁶¹ Rose, G., *Sprechsaal*, 62, 314, 333, 352, 375 (1929); *Chem. Abs.*, 23, 4544 (1929).

⁶² German P. 493,857, Dec. 30, 1925, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, 27, 578 (1933).

⁶³ German P. 528,394, July 9, 1929, to Deutsche Spiegelglas A.-G.

⁶⁴ German P. 524,374, May 10, 1927, to Deutsche Spiegelglas A.-G.

⁶⁵ Vargin, V. V., *Keram. i Steklo*, 7, No. 1, 4 (1931); Wollner, F., Wollner, R., and Nikolai, F., British P. 339,903, March 12, 1929; Austrian P. 120,674, Oct. 15, 1929; French P. 691,805, March 12, 1930.

⁶⁶ Jaeckel, G., German P. 583,001, Aug. 26, 1933, to Sendlinger optische Glaswerke; *Chem. Abs.*, 28, 277 (1934).

⁶⁷ British P. 440,778, Jan. 6, 1936, to N. V. Philips' Gloeilampenfabrieken; see also, Elenbaas, W., Jonas, G. B., and van Wyk, A., Canadian P. 373,786, May 17, 1938; *Chem. Abs.*, 32, 5316 (1938).

⁶⁸ Smelt, J. A. M., U. S. P. 2,056,627, Oct. 6, 1936; *Chem. Abs.*, 30, 8550 (1936).

⁶⁹ Heyne, G., *Angew. Chem.*, 46, 473 (1933); Salmons-Karsten, A., *Skizzen Rorhiedy*, 11, 35 (1934); *Chem. Abs.*, 29, 6713 (1935).

and Wellmann⁷⁰ have suggested alkali-beryllium-borate glasses as substitutes for quartz in optical work. Such a glass, containing 15 to 25 parts of boric acid, 1 to 2 of beryllium carbonate and an alkali carbonate equivalent to 3 to 6 parts of lithium carbonate, is reported to be applicable for lenses, prisms and mercury-vapor lamps. Draibach and Draibach⁷¹ fuse beryllium ortho- or meta-phosphate, and add the corresponding salts of calcium, magnesium or sodium.

Another trend is the development of lithium-beryllium-borate "Getan" glass, which is not hygroscopic and does not decompose in the air, but is transparent to ultraviolet and x-rays.⁷² One mm. of the glass transmits 80 per cent of the energy of the wave-length 2537A.

The Philips Lamp Co.⁷³ suggest for bulbs for transmitting ultraviolet a clear, transparent glass containing a fluoride and practically free from lead, antimony or titanium. Locke and Locke⁷⁴ melt a fluorine-containing batch (SiO_2 35.5-40, H_3BO_3 16.5-32.5, Al_2O_3 21-27 and CaO 11-17 per cent with calcium fluoride) in a carboniferous container. Fuwa and Suzuki⁷⁵ use 1 to 5 per cent sodium fluoride and 1 to 5 per cent ammonium oxalate or tartrate.

A glass of high resistance to water and permeable to the ultraviolet may be composed for the greater part of barium metaphosphate, along with metaphosphates of calcium and magnesium.⁷⁶ Grimm and Huppert⁷⁷ replace the silica normally used in making glass wholly or in part by AlPO_4 in the proportion of one molecule for every two of silica replaced. Ammonium salts, particularly phosphates, may be added to the frits of phosphate glass.⁷⁸

Other Ultraviolet-Transmitting Materials. In the preparation of window-glass substitutes, materials quite unlike glass have at times been employed. Thus a urea-formaldehyde condensation product was introduced for this purpose by the Lucio Products Corporation under the name of Aldur. Crist⁷⁹ gave a curve for its transmission and compared it with "Vitaglass." (Figure 87.) He found also that when exposed at 65°C. at 8 inches from a 220-volt mercury lamp, no change in transmission of the 3020A region was apparent after 41 hours, a fairly severe test. The transmission of the 2540A line was decreased from 48 to 40 per cent in 18 hours. Data for "Plexiglas" (Acryloid) have been given by Jakobson.⁸⁰

A filter suitable for glazing windows which transmits to 2900A is a polymerized vinyl acetate, reinforced with a reticulated material as a wire mesh or woven

⁷⁰ Ziegler, W., and Wellmann, M., *Z. tech. Physik*, 14, 288 (1933); *Chem. Abs.*, 27, 4366 (1933); Wellmann, M., German P. 585,816 (1933); *Chem. Abs.*, 28, 1492 (1934).

⁷¹ Draibach, H., and Draibach, F., British P. 436,426, Oct. 10, 1935; French P. 785,966, Aug. 23, 1935.

⁷² Hertariken, S. D., *Tech. Phys. U.S.S.R.*, 3, 336 (1936); *Chem. Abs.*, 31, 4782 (1937).

⁷³ British P. 373,378, May 29, 1930, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, 27, 3306 (1933).

⁷⁴ Locke, F. M., and Locke, F. J., U. S. P. 1,886,280, Nov. 1, 1932, to Corning Glass Co.; *Chem. Abs.*, 27, 1470 (1933).

⁷⁵ Fuwa, K., and Suzuki, S. Japanese P. 101,817, July 1, 1933; *Chem. Abs.*, 28, 5617 (1934); Fuwa, K., U. S. P. 1,971,309, Aug. 21, 1934, to General Electric Co.; *Chem. Abs.*, 28, 6542 (1934).

⁷⁶ French P. 751,524, Sept. 5, 1933, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 28, 1159 (1934); Kaufmann, W., and Bungartz, E., U. S. P. 2,031,958; German P. 634,698-9 and 636,035; *Chem. Abs.*, 31, 828 (1937). Aluminum may also be added to increase the water resistance.

⁷⁷ Grimm, H. G., and Huppert, P., German P. 580,295, July 8, 1933; *Chem. Abs.*, 27, 388, 4895 (1933).

⁷⁸ French P. 775,451, Dec. 28, 1934, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 29, 2680 (1935); British P. 424,366, Feb. 20, 1935. For other patents on ultraviolet glasses, see German P. 527,053, Dec. 16, 1928, to Deutsche Gasglühlicht Auer-Ges.; Gericke, I., German P. 527,404, Jan. 17, 1930; Weid, H. W., U. S. P. 1,845,376, Feb. 16, 1932; *Chem. Abs.*, 26, 2294 (1932).

⁷⁹ Crist, R. H., *Ind. Eng. Chem.*, 20, 1367 (1928); see also Katowaki, H., and Kasai, E., *Repts. Imp. Ind. Research Inst., Osaka*, 13, No. 3 (1932); *Chem. Abs.*, 27, 1719 (1933).

⁸⁰ Jakobson, T., *Tek. Tid.*, 67, Uppl. A-C, Kemi, 15 (1937); *Chem. Abs.*, 31, 4210 (1937).

fabric.⁸¹ It has been proposed to make a fabric of threads formed of a core of material opaque to light, such as cotton, carrying a coating such as regenerated cellulose, capable of transmitting ultraviolet.⁸² The Vitalite Co. produces a fine wire cloth coated with a cellulose acetate composition, yielding a flexible wire product, possessing the advantages of weather resistance and transmitting the ultraviolet range. Ramstetter⁸³ suggested the use of transparent condensation products of carbamide and its derivatives with substances capable of yielding formaldehyde as a substitute for quartz glass; the condensation products absorb ultraviolet rays but slightly. Walsh⁸⁴ coats a wire cloth with an ultraviolet-transparent film of cellulose acetate 100, triphenyl phosphate 10-20 and dibutyl tartrate 10 to 20 parts.

In some instances⁸⁵ "Vitaglass" or quartz glass may be made into a laminated glass by the aid of acetylcellulose applied in the form of thin sheets. Zimmerli⁸⁶ prepared an ultraviolet-transmitting material by evaporation of a cellulose ester and a plasticizer, such as diethyl phthalate. Polymerized vinyl compounds, including vinyl acetate, chloroacetate and styrene, may be used in single or laminated sheets in making reinforced glass substitutes permeable to ultraviolet light.⁸⁷

Data on the Transmission of Various Ultraviolet-permeable Materials.

Starkie and Turner⁸⁸ determined the transmissions of 2 mm. thicknesses of eight commercial glasses over the range 7000 to 2000Å. Corex A was found to transmit 89 per cent in the therapeutic region (2950-3150Å). The remaining glasses showed: "Sanalux," 73 per cent, "Sun Ray" 62, "Holvi" 61, "Viat" 54, "Helio" 53, "Uviol" 45, "Quartz-Lite," 4 per cent. Ordinary window glass transmits only 1 per cent of these rays. Corex had the lowest iron content, 0.012 per cent, that of the remaining samples ranging from 0.021 to 0.054 per cent. After a 12 weeks' exposure to sunlight, Corex became stained with a white film. But on being cleaned, it showed undiminished transmission. When artificially aged under the carbon arc, the greatest change occurred in the first two hours, the fall in transmission coinciding with a decrease in the proportion of ferrous oxide to total iron oxide in the glass. Turner⁸⁹ finds this change can be reversed by heating the glass to 600-700°C.⁹⁰ Hoffman⁹¹ believes the solarization to involve the formation of ferrites.

According to Bundesen, Lemon, Falk and Coade,⁹² incandescent 300-watt lamps with ordinary glass bulbs emitted radiations comparable to Chicago sunlight in the winter months and Vitaglass bulbs emitted radiations as far as the region 2800 to 2900Å.

The results of the physical transmission of Corex received confirmation in

⁸¹ Greider, C. E., U. S. P. 1,786,205, Dec. 23, 1930, to National Carbon Co. Note also British P. 366,077, June 29, 1929.

⁸² Millen, J., U. S. P. 1,910,850, May 25, 1933; *Chem. Abs.*, 27, 4101 (1933).

⁸³ Ramstetter, H., German P. 416,753, Jan. 31, 1923, to Badische Anilin und Soda Fabrik.

⁸⁴ Walsh, J. F., U. S. P. 1,931,518, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, 28, 637 (1934).

⁸⁵ Colefax, M. A., British P. 323,671, *Kunststoffe*, June, 139 (1930). Dreyfus, C., U. S. P. 1,924,398, Aug. 29, 1933; *Chem. Abs.*, 27, 5503 (1933); U. S. P. 2,002,082, May 21, 1935; *Chem. Abs.*, 29, 4539 (1935); Canadian P. 330,842, *Chem. Abs.*, 27, 3375 (1933); British P. 306,397, Feb. 18, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 23, 5021 (1929).

⁸⁶ Zimmerli, A., U. S. P. 1,842,640, Jan. 26, 1932, to Acetol Products; *Chem. Abs.*, 26, 1781 (1932).

⁸⁷ British P. 366,077, July 29, 1929, to Celluloid Corp.; *Chem. Abs.*, 27, 3047 (1933).

⁸⁸ Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, 12, 306 (1928); *J. Soc. Chem. Ind. Supplement*, March 29, 245 (1929). Other data have been given by Winther, C., *Z. wiss. Phot.*, 25, 230 (1928), and by Harris, D. T., *J. Sci. Instruments*, 6, 2 (1929).

⁸⁹ Turner, W. E. S., *J. Soc. Chem. Ind.*, 48, 65 (1929).

⁹⁰ Compare Hood, H. P., U. S. P. 1,889,067, Nov. 29, 1932; *Chem. Abs.*, 27, 1470 (1933). British P. 298,908, Nov. 14, 1928, to Corning Glass Co., *Chem. Abs.*, 23, 3066 (1929). Hood heats to 550° for 15 minutes or to 400°C. for one hour.

⁹¹ Hoffmann, J., *Glastech. Ber.*, 12, 53 (1934); *Chem. Abs.*, 28, 4554 (1934).

⁹² Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assoc.*, 89, 187 (1928).

prophylactic animal tests against rickets, using Uviarc irradiation through the samples.⁹³ Growth curves, calcium and phosphorus determinations in the blood serum, x-rays of the tibiae and femurs, bone ash and pathological studies agreed in showing that irradiation through Corex was as effective as direct irradiation. "Vitaglass" was less effective and animals irradiated through ordinary window glass gave results very similar to those found in non-irradiated animals. Wyman⁹⁴ also conducted therapeutic tests on rachitic children with similar results.

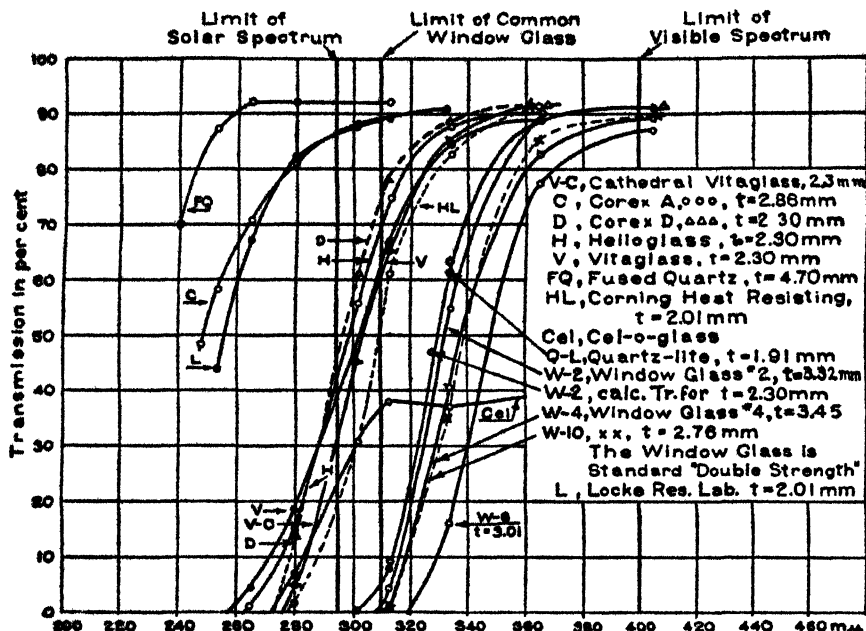


FIGURE 88. Transmission Curves of Ultraviolet-permeable Glasses.
(Coblentz and Stair, *Journal Research, Bureau of Standards*).

Durability of Ultraviolet-transmitting Materials. The question of solarization, or the effect of prolonged exposure to the sun or other sources of ultraviolet is of importance since ultraviolet transmitting materials are intended for use over long periods. The discoloration of glass in the globes surrounding street arc lights is familiar to everyone. Eckert⁹⁵ noted that glasses containing a small percentage of cerium rapidly assume a brown color in day or artificial light due to the action of ultraviolet rays, the glass becoming fluorescent and phosphorescent. The brown color fades irreversibly on heating.

In 1927 the Bureau of Standards had found that nearly all of the glasses then in use undergo a photochemical action, the glass decreasing greatly in transparency in the region 2900 to 3100Å when exposed to ultraviolet radiations.⁹⁶ The mate-

⁹³ Wyman, E. T., Holmes, A. D., Smith, L. W., Stockbarger, D. C., and Piggott, M. G., *Am. J. Diseases of Children*, 37, 473 (1929); *Chem. Abs.*, 23, 3064 (1929).

⁹⁴ Wyman, E. T., *Boston Med. & Surg. J.*, 197, 376 (1927).

⁹⁵ Eckert, F., *Z. tech. Physik*, 7, 300 (1926); Eckert, F., and Schmidt, K., *Glastech. Ber.*, 10, 80 (1932); *Chem. Abs.*, 27, 1468 (1933).

⁹⁶ Bureau of Standards, *J. Frank. Inst.*, 666 (1927); *Letter Circular No. 235, 3rd Revision*; *J. Research Bur. Standards*, 3, 629 (1929); Coblentz, W. W., and Stair, R., *Trans. Illum. Eng. Soc.*, 23, 1121 (1928); *Chem. Abs.*, 23, 944 (1929).

rials fell into three classes (Figure 88): (1) Fused quartz, Corex and Locke glass, which have an initial transmission of the 3020A line of over 85 per cent and show little or no decrease in solarization; (2) "Vitaglass" and Helioglass, with initial transmission of 45-55 per cent, decreasing to about half on exposure; (3) Quartz-lite and common window glass, with initial transmissions of 0 to 1.5 per cent and no change on exposure. Cel-O-glass becomes opaque to this line after 25 hours' exposure to the quartz mercury arc, but a sample that had been exposed to the sun for 400 hours during the months of April to October decreased but little in transparency. On the other hand, samples that had transmitted 30 per cent when new, transmitted only 5 to 10 per cent after having been exposed on the side of a building day and night from April to December, showing that the change in transparency may depend upon weather conditions. This product has been employed in poultry houses for preventing leg weakness in chicks.⁹⁷ Russell and Howard⁹⁸ found that the value of Cel-O-glass for this purpose was not diminished after exposure for 13.5 months.

In more recent work, Coblenz⁹⁹ reported improvement in the quality of certain of these glasses. He summarized data (based on samples secured prior to May 1, 1930) based on exposure of the glasses for ten hours at 15 cm. from a 110-volt, horizontal Uviarc and of duplicate samples exposed to the sun for five to twelve months, using an average thickness of 2.3 mm. (Table 15.)

Table 15.—Transmission of Ultraviolet Rays by Glass.

Trade Name	Number of Samples	Average Per Cent Transmission—		
		New	After Uviarc	After Sun
Quartz glass	1	92	92	92
Corex D	3	61	59	60
Newglas	3	63	50	57
Uviol-Jena	3	67	48	53
Helioglass	8	64	45	53
Sunlit	3	71*	42*	51
Vitaglass	20	58	33	42
Common window	3	0	0	0

* Improved material later examined averaged 72 per cent when new and 47 per cent after exposure to the mercury lamp.

Rüttenauer¹⁰⁰ found the foreign products Osram UV, Ultraviol, Brephos, Bios, Vita and Schott's UV to show only small ageing. He has also considered the effect of heat on the rate of ageing, a matter of importance when such glasses are used in lamp bulbs. Nitchie and Schmutz¹⁰¹ found in some cases an increase in short-wave transmission at 450°C.

Coblenz and Stair¹⁰² studied the effects of various filtered ultraviolet wavelengths in producing changes in the ultraviolet transmission of soda-lime-silica glass. The work was done in the hope of accelerating stabilization of the transmission. This effort proved impracticable because of antagonistic effects about 3650A which

⁹⁷ Cochran, R. L., and Bittenbender, H. A., *Bull.* 246, *Iowa State College, Agr. Expt. Sta.*, 1928.

⁹⁸ Russell, W. C., and Howard, C. H., *Poultry Sci.*, 8, 290 (1929).

⁹⁹ Coblenz, W. W., *Trans. Illum. Eng. Soc.*, 26, 610 (1931).

¹⁰⁰ Rüttenauer, A., *Sprechsaal*, 61, 449 (1928).

¹⁰¹ Nitchie, C. C., and Schmutz, F. C., *Science*, 71, 590 (1930).

¹⁰² Coblenz, W. W., and Stair, R., *J. Research Bur. Standards*, 13, 773 (1934); *Proc. Nat. Acad. Sci.*, 20, 630 (1934); *Chem. Abs.*, 29, 1597 (1935).

reversed the action of shorter wave-lengths. No wave-length shorter than 3650A was found to have the exclusive property of increasing or decreasing the ultraviolet transmission of these glasses. A phosphate-lime glass has its transmission lowered by wave-lengths shorter than 2900A, and this could not be retarded by exposure to the region 2970-3650A, in contrast to the soda-lime-silica glasses. Stockbarger¹⁰⁸ is of the opinion that solarization, at least so far as it relates to the application of ultraviolet glasses in photochemical apparatus, is not serious. Solarization takes place within a short length of time, after which the characteristic properties of the glass are retained for a considerable time. It has been said that when kept in the dark, glass, previously solarized by the mercury arc, does not regain any of its lost ultraviolet transparency, but that it does regain transparency when exposed to sunlight directly or through window glass or when exposed to the mercury arc through a thick layer of window glass. It is also pointed out¹⁰⁴ that the use of the mercury-vapor lamp to predict the loss of transparency of glass when exposed to sunlight may give misleading results.

The tendency of an ultraviolet-permeable glass to lose transparency may be counteracted by the incorporation of a small proportion (0.05-0.5 per cent) of manganese oxide.¹⁰⁵ The I. G. Farbenindustrie¹⁰⁶ describes an ultraviolet-permeable phosphate glass (stable to irradiation) which was said to have the following composition: potassium carbonate 13.77, potassium nitrate 6.71, calcium carbonate 8.93, barium carbonate 3.22, magnesium carbonate 18.53, B₂O₃ 31.04, alumina 28.80 and secondary ammonium phosphate 48.70 parts. Huppert and Wolff¹⁰⁷ state that the important phosphatic glasses may be rendered more stable to radiations by including an ammonium salt (phosphate, carbonate or nitrate). The formation of blisters may be avoided by the addition of an oxidizing agent.

Lasse¹⁰⁸ finds irradiation of ordinary and Uviol plate glass with wave-lengths 3000 to 4000A from a Hanau silica burner diminishes the transparency for these rays to 34 and 19 per cent respectively. The coloration of manganese-containing glass by ultraviolet rays is said by Cross¹⁰⁹ to be due to light of a wave-length only slightly greater than 2900A, the absorption limit of the glass. The tinting takes place only near the surface, and is hastened by heating. Decolorization is accelerated by heat or visible light.

The fluorescent effects produced by ultraviolet on various glasses are sufficiently different to afford indications of the nature of their coloring materials.¹¹⁰ Shrum, Patten and Smith¹¹¹ found heat treatment at 300°C. to remove the ability of ultraviolet light or even x-ray solarized glasses to luminesce before the quartz mercury arc. The transmission in the ultraviolet was restored as the thermoluminescence disappeared.¹¹²

¹⁰⁸ Stockbarger, D. C., *Science*, **70**, 73 (1929).

¹⁰⁴ Wood, A. R., and Leathwood, M. N., *Nature*, **124**, 441 (1929).

¹⁰⁵ British P. 291,468, June 4, 1927, to Soc. Anon. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny, et Cirey; *Chem. Abs.*, **23**, 1235 (1929); *Brit. Chem. Abs.*, **B**, 145 (1930); French P. 647,188, June 4, 1927; Long, B., U. S. P. 1,779,176.

¹⁰⁶ British P. 424,366, Dec. 2, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 406 (1935).

¹⁰⁷ Huppert, P., and Wolff, H., German P. 630,347, Oct. 19, 1935; U. S. P. 2,077,481; see also Hoffmann, J., *Sprechsaal*, **70**, 517, 529 (1937); *Chem. Abs.*, **32**, 5592, 8717 (1938).

¹⁰⁸ Lasse, R., *Helv. Phys. Acta*, **5**, 92 (1932); *Chem. Abs.*, **26**, 6086 (1932).

¹⁰⁹ Cross, C. L., *Phys. Rev.*, **27**, 108 (1926).

¹¹⁰ Lester, W. R., *Glass Ind.*, **12**, 83 (1931).

¹¹¹ Shrum, G. M., Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada*, **22**, (3), 433 (1928); *Chem. Abs.*, **23**, 2003 (1929).

¹¹² For further discussion of the theory of solarization processes, see Klemm, A., and Berger, E., *Glastech. Ber.*, **13**, 349 (1935); Hoffmann, J., *Ibid.*, **12**, 53 (1934); *Chem. Abs.*, **28**, 4554 (1934); *Glastech. Ber.*, **13**, 47 (1935); *Brit. Chem. Abs.*, **B**, 1093 (1936); *Glastech. Ber.*, **14**, 281 (1936); *Glass*, **13**, 419, 433 (1936).

FILTERS

In the visible region, a great number of screens or filters have been prepared for the isolation of definite wave-length regions; certain of these find wide employment in photography, especially in color photography. Others are of importance in stage lighting. The properties of these and other filters are due to the ability of the substances employed to absorb radiations of definite frequencies selectively. Substances which are highly absorbing even when present in extremely dilute solutions are the most satisfactory materials for filters since, when taken in higher concentrations, they exhibit a sharp cut-off of radiations transmitted. This means that the wave-length range between nearly complete transmission and nearly complete absorption is very narrow, comprising only a few Angström units. Since but few substances meet this requirement, filters are best used with discontinuous line sources of radiations as the mercury arc.

The theory of the application of glass filters to the measurement of the intensity of groups of lines emitted by a source has been discussed in detail by Stockbarger and Burns.¹¹⁸ Errors may arise because of failure to take into account the fact that the transmission curves of filters are not rectangular but sloping; if the cut-off be taken as the wave-length at which the transmission becomes zero, the results will be greatly in error. These authors recommend that the effective "cut-off" be considered to be the point at which the energy transmitted by the filter below the "cut-off" equals that which is selectively absorbed above it. In order to locate this point there needs to be known, besides the transmission characteristics of the filter, the energy distribution of the source in the region in which the filter transmits poorly.

Particular attention has been devoted to the theory relating the slope of the absorption curve of a filter material to the effectiveness with which it will separate a given line from close neighboring lines, by Dahm,¹¹⁴ who was especially interested in developing filters suitable for use in studies of the photoelectric effect. He gives absorption data for over twenty organic compounds, plotted in an unusual manner adapted to his theoretical treatment.

Stability is another quality desired in a filter material. The absorbed radiations must produce or initiate only very slow photochemical changes. Otherwise, the nature of the filtering material will change during its use, and the products formed may absorb quite differently, resulting in a change in the filtering properties with use. In the colored filters employed in the visible region, these changes are usually slow enough so that the filters are stable for considerable periods. Liquid filters composed of solutions of colored salts or dyes in cells with parallel glass sides, or solid filters of glass or stained films of collodion or more usually gelatin, are commonly employed. Simple inorganic salts when available are usually more stable and more readily prepared in definite concentrations than are the organic dyes, which may be of less definite purity and which are frequently subject to fading.

In the ultraviolet region, the energies associated with the various wave-lengths absorbed by the filters are far greater than in the visible region. In this region, therefore, it is necessary to check the filtering characteristics of filters at frequent intervals or else to use solutions which flow slowly through the filter cells.

Filters capable of transmitting only narrow spectral bands or individual lines are rare. It is usually necessary to use filters to supply radiations from which certain more or less broad spectral regions have been excluded. In the visible region, there is a filter arrangement which transmits only the green line of the mercury arc. This filter is didymium glass, which has a sharp absorption band

¹¹⁸ Stockbarger, D. C., and Burns, L., *Phys. Rev.*, **34**, 1265 (1929).

¹¹⁴ Dahm, T. M., *J. Opt. Soc. Am.*, **15**, 266 (1927).

between 5500 and 5800Å. Used with a strong yellow filter, the filter yields the green line in high intensity and supplies a strong source of nearly monochromatic light. Glasses to emphasize color contrasts may contain neodymium oxide.¹¹⁵ A discussion of filters in the infrared and visible regions lies beyond the scope of this book.¹¹⁶ Many photographic filters have the drawback of fluorescing and so causing a loss of contrast.¹¹⁷

Filters for Black Light. Among the earliest ultraviolet filters were those designed to exclude the visible rays and transmit only the invisible ultraviolet. Such filters have recently acquired new importance with the development of methods of fluorescence analysis under ultraviolet irradiation. By their use, fluorescent effects in great variety are easily secured. In a darkened room irradiated only by ultraviolet rays, the teeth, eyes and even the fingernails glow with a weird yellowish fluorescence. Artificial teeth do not become fluorescent but appear black. The beautiful fluorescent effects characteristic of various minerals have been so frequently exhibited in museums as to be familiar to almost everyone. Uranium nitrate shines when exposed to ultraviolet rays, and vapors of mercury may be seen rising from a body of mercury even at room temperature when photographed by ultraviolet rays.

A filter for this purpose consisting of quartz coated with silver was employed by R. W. Wood in 1911 in a demonstration at the Royal Institution of the fluorescent effects produced by ultraviolet radiations. Among the striking effects there demonstrated was the fact that white zinc oxide comes out black. Photographs of flowers taken through a quartz lens were also exhibited. A number of flowers which, when photographed by visible light, came out in widely different shades, when white or colored, left a black or dark gray image when photographed by ultraviolet light. Another group of flowers to which Michaud and Tristan¹¹⁸ gave the name of ultraviolet flowers, were reproduced by ultraviolet much as by ordinary light. These flowers were yellow under ordinary light. These authors prepared a lens which excludes light other than ultraviolet by precipitating on a quartz lens a layer of silver from an alkaline silver solution by means of a 10 per cent solution of milk sugar.

Silver, either in the form of plates or in the colloidal state, is not entirely satisfactory since its absorbing capacity ends at about 4000Å¹¹⁹ and with high concentrations of silver, absorption in the short ultraviolet region is noted. Brock¹²⁰ prepared a silver filter by exposing a lantern slide, developing it to a brown color and then stripping off the emulsion and supporting the latter between two plates of Uviol or "Vitaglass." The resulting filtering action is believed superior to that of either sputtered or chemically deposited films, maximum transmission occurring at about 3000Å.

Wood¹²¹ suggested the use of nitroso-dimethylaniline in making filters transparent only to ultraviolet rays. This compound, however, transmits only the longer

¹¹⁵ Weidert, F., *British P.* 338,334, Dec. 15, 1928; *Chem. Abs.*, 25, 2259 (1931).

¹¹⁶ See Mees, C. E. K., in Glazebrook's *Dictionary of Applied Physics*, IV; Potapenko, G., *J. Russian Phys. Chem. Soc.*, 48, 790 (1916); *Brit. J. Phot.*, 68, 507 (1921).

¹¹⁷ Bäckström, H., and Johansson, R., *Z. wiss. Phot.*, 36, 194 (1937); *Chem. Abs.*, 31, 6123 (1937); 32, 2837 (1938).

¹¹⁸ Michaud, G., and Tristan, F., *Scientific American*, 111, 301 (1914).

¹¹⁹ See also Goos, F., *Z. Physik*, 100, 95 (1936); for gold films, see Goos, F., *Z. Physik*, 100, 606 (1937).

¹²⁰ Brock, G. C., *Sci. Proc. Roy. Dublin Soc.*, 20, 563 (1933); *Brit. J. Phot.*, 80, 495 (1933); *Chem. Abs.*, 27, 5262 (1933).

¹²¹ Wood, R. W., *Phil. Mag.*, 5, 257 (1903); see also Lehmann, H. *Physik. Z.*, 11, 1039 (1910).

ultraviolet. Absorption spectra for the aniline derivative and for methyl violet have been determined by Pospelov and Yampolskii.¹²²

Winther and Mynster¹²³ suggested a filter which transmits a range of 4050 to 3200Å with a maximum at 3750Å. It consists of a one centimeter cell containing a 2.5 per cent solution of copper sulfate with six times the quantity of ammonia necessary to redissolve the precipitate which first forms. This is combined with a one centimeter cell of a 0.045 per cent solution of fuchsine in water. In another filter, the dye is replaced by a 0.1215 per cent solution of potassium chromate, the maximum transmission in this case being at 3130Å. With an increasing excess of ammonia, copper sulfate solution becomes more transparent, especially in the ultraviolet; the maximum transparency is attained when the ammonia present is four times the quantity necessary to redissolve the precipitated copper hydroxide, and then extends from 4500 to 3000Å.

Lamps in Corex are made impermeable to visible rays, while retaining their ultraviolet transmission, by dipping in an alcoholic suspension of P_2O_5 68, CaO 27, B_2O_3 5 per cent, with cobalt oxide to color, or of SiO_2 68.5, B_2O_3 23, Na_2O 6.5 and Al_2O_3 2 per cent. The lamps are then heated in a furnace.¹²⁴ An envelope to serve this same purpose has been suggested by Gillard and West.¹²⁵ It comprises glass with nickel oxide and a little copper oxide. The maximum transparency is at 3650Å, falling rapidly on either side of this wave-length. Another means of securing ultraviolet radiation with but one per cent of the visible is by operation of a small mercury arc at 5 amperes and 15 volts.¹²⁶

Filters Excluding Various Ultraviolet Regions. Some of the glasses whose transmission characteristics have been discussed in the preceding section, have been employed as filters for various wave-lengths in the ultraviolet region. Their usefulness for this purpose is somewhat limited by the lack of sharpness of their transmission curves.¹²⁷

Corning glass filters¹²⁸ are most satisfactory where their thickness and consequent bulk are not objectionable, and where appreciable heat must be dealt with. As is apparent from Figure 89, they generally have rather broad but high transmission characteristics and hence are used in combination to secure the desired effects. A nickel oxide glass (Corning) transmits 3660Å. Further data on the filtering properties of various glasses by Taylor and Holladay are recorded in Figure 90.¹²⁹

In order to prepare a ray filter which will allow only waves of a definite length to pass, Peskov¹³⁰ states that it is necessary to calculate the coefficient of absorption of the substance and then determine the density and thickness of the solution so that the desired quantity of energy of a definite wave-length will pass the filter.

Gases have been widely used as filters in the ultraviolet. The coefficients of absorption of a number of gases for light after passage through quartz windows has been measured by Varley.¹³¹ It is the filtering characteristic of oxygen (aside

¹²² Pospelov, A., and Yampolskii, B., *J. Phys. Chem. (U.S.S.R.)*, **3**, 514 (1932); *Chem. Abs.*, **27**, 1826 (1933).

¹²³ Winther, C., and Mynster, E. H., *Z. wiss. Phot.*, **24**, 90 (1926); *Chem. Abs.*, **20**, 3249 (1926).

¹²⁴ French P. 762,053, April 3, 1934, to Compagnie des lampes. See also Eidinow, A., and Hewitt Electric Co., Ltd., British P. 307,961, Dec. 13, 1927; *Chem. Abs.*, **24**, 29 (1930).

¹²⁵ Gillard, F. W., and West, D. L., British P. 294,949, Apr. 1, 1929; *Chem. Abs.*, **23**, 1827 (1929). Note also Sugie, J., *J. Japan. Ceram. Assoc.*, **34**, 24 (1926); *Chem. Abs.*, **22**, 487 (1928).

¹²⁶ Zahour, R. L., *Elec. J.*, **30**, 453 (1933).

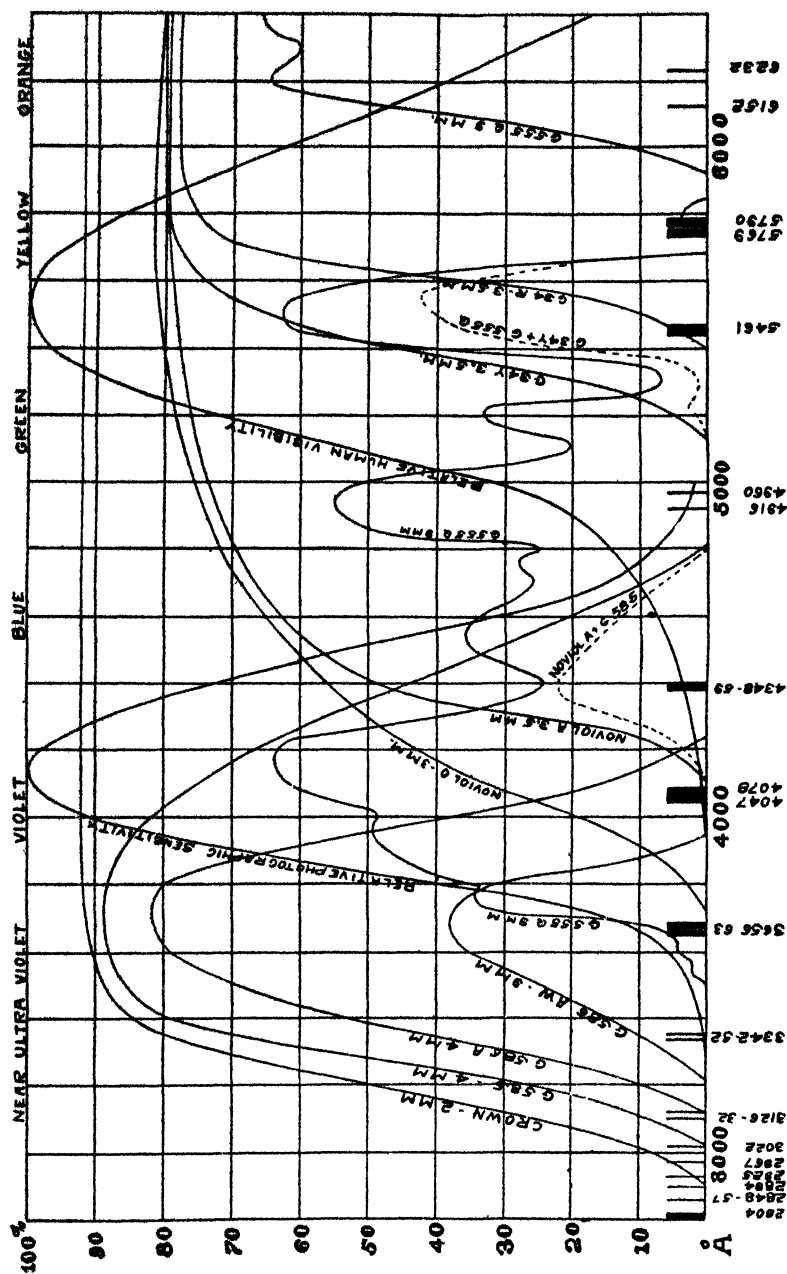
¹²⁷ Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).

¹²⁸ Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech. Papers*, 119 (1919); 148 (1920); *Sci. Paper* 325 (1918).

¹²⁹ Taylor, A. H., and Holladay, L. I., *Trans. Illumin. Eng. Soc.*, **26**, 711 (1931).

¹³⁰ Peskov, N. P., *J. Phys. Chem.*, **21**, 381 (1917); *Z. wiss. Phot.*, **18**, 235 (1919).

¹³¹ Varley, W. M., *Proc. Camb. Phil. Soc.*, **12**, 510 (1904).



CORNING FILTERS - DATA FROM CORNING GLASS WORKS AND BUREAU OF STANDARDS.

(Courtesy, Cooper-Hewitt Electric Co.)

FIGURE 89. Transmission Curves for Corning Filters.

from the limitations of the output of the source employed) which sets the short wave limit in most photochemical work, since it begins to absorb strongly at 1860A, while nitrogen is transparent even at 1250A. According to Peskov, chlorine is frequently useful, since its maximum absorption is in the region 3800-3000A. Bromine vapor cuts out the visible part of the spectrum to 3800A and its absorption capacity ends slightly beyond the point where chlorine absorption begins.¹³² In water solutions, the absorption characteristics of these two elements change because of the formation of complex molecules of halogen and water.

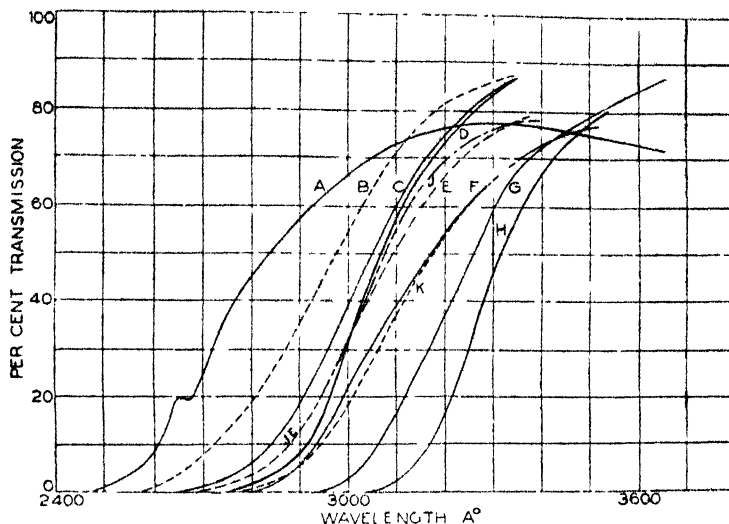


FIGURE 90. Spectral Transmission Curves of Glass Filters (Taylor and Holladay, *Transactions Illumination Engineering Society*). A, red-purple Corex A, 4.21 mm. thick; B, microscope glass, 0.18 mm.; C, microscope slide, 0.96 mm.; D, "Pyrex," 1.05 mm.; E, 2 layers of microscope glass, 0.36 mm. total; F, 3 layers of microscope glass, 0.55 mm. total; G, "Pyrex," 2.99 mm.; H, Quartzlite, 2.02 mm.; J, Helioglass, 2 mm.; K, "Vitaglass," 2.77 mm.

Use has been made of chlorine and bromine filters in the work of Svedberg and Nichols¹³³ on the determination of the molecular weight of egg albumin by ultracentrifugal methods. In this work, it was necessary to determine the concentration of the protein solution at various parts of a quartz cell by a photographic method depending upon the property of the protein to absorb in the ultraviolet. In order to measure the concentration of the protein by means of the density of a photograph obtained by passing light from a mercury arc through the solution, it is necessary that a strong absorption band of the protein be used. Since the protein does not absorb much light of wave-lengths longer than about 2950A, it is necessary that such light be removed by a filter to prevent the light from affecting the photographic plate. A combination of chlorine and bromine filters absorbs most rays longer than 2950A and passes those shorter. Although the filter does not remove the yellow mercury line, this does not affect the photographic plate.

To obtain the 2537A line alone by methods other than the use of special reso-

¹³² Oldenberg, O., *Z. Physik*, **29**, 328 (1924).

¹³³ Svedberg, T., and Nichols, J. B., *J. Am. Chem. Soc.*, **48**, 3085 (1926).

nance lamps, it has been proposed to use the halogens at higher concentrations. Peskov¹³⁴ calculated from their extinction coefficients that the bromine should be about 0.0046 molar and the chlorine 0.176 molar or about 4 atmospheres. Oldenberg¹³⁵ proposed to avoid any absorption of the 2537A line by bromine¹³⁶ by omitting the latter and employing chlorine at a pressure of 6.5 atmospheres. Such high-pressure filter cells have been constructed of quartz. The absorption of the chlorine filter has been measured by Villars.¹³⁷ Calculations showed the Peskov filter would be the more nearly monochromatic and would transmit about 27 per cent of the light incident at 2537A. Taylor¹³⁸ states that filters (not at high pressure) of chlorine gas or of chlorine in carbon tetrachloride show a decreasing absorptior per unit with increasing thickness and that the decrease is not exponential. The last small per cent of actinic light is difficult to remove.

As a filter for altering the intensity of the 2537A line, Melville and Walls¹³⁹ propose sulfur-free carbon tetrachloride mixed with purified hexane or preferably cyclohexane. Such filters show decomposition after 15 minutes.

The mercury arc has another strong line at 3650A. Filters for isolation of this line have been proposed by Hartmann,¹⁴⁰ Luther and Forbes,¹⁴¹ Winther,¹⁴² Andrich and Le Blanc,¹⁴³ and Buttolph.¹⁴⁴ Absorption data regarding the Luther-Forbes filter (0.78 cm. of a solution containing 0.0785 g. fuchsine S, 0.0164 g. methylene blue, 0.0410 g. *p*-nitrosodimethylaniline per liter) and the Winther filter (1 cm. of 0.03-per cent aqueous Diamant Fuchsine) have been given by Gray.¹⁴⁵ The former gave in a 1-cm. layer a maximum transmission of 8 per cent at 3650A. In one-fifth strength, 2 cm. transmitted 30 per cent. Acids and alkalis alter absorption by the Luther-Forbes filter, as well as that of the Winther filter. It is the opinion of Potapenko¹⁴⁶ that the most suitable form of light filter for Uviol lamps is a stained gelatin film, which may be prepared by coating glass with a gelatin solution containing the desired dye, and after drying, stripping the film so formed. A list of dyes for various wave-lengths was given by Miethe and Stenger¹⁴⁷ and by Mannich.¹⁴⁸ Staats¹⁴⁹ has discussed the problem of making monochromatic glass filters for the wave-lengths 1014, 578, 546, 436, 405, and 365 mμ of the mercury arc. In each, two components are used, (a) a glass which absorbs with sharp cut-off, all radiations of wave-length shorter than the one it is desired to transmit and (b) one with a similar absorption for longer wave-lengths. The ratio of the thicknesses of the two components is specified for each filter. Graphs give the variation in transmission and purity of the transmitted light for each of 15 combinations. In some, auxiliary filters are required. Since the characteristics of such filters depend upon the spectral distribution of the source and the sensitivities of the

¹³⁴ Peskov, N. P., *Z. wiss. Phot.*, **18**, 235 (1919); *J. Russ. Phys.-Chem. Soc.*, **47**, 918 (1915).

¹³⁵ Oldenberg, O., *Z. Physik*, **29**, 328 (1924).

¹³⁶ Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916).

¹³⁷ Villars, D. S., *J. Am. Chem. Soc.*, **48**, 1874 (1926).

¹³⁸ Taylor, W., *Nature*, **118**, 697 (1926).

¹³⁹ Melville, H. W., and Walls, H. J., *Trans. Faraday Soc.*, **29**, 1255 (1933).

¹⁴⁰ Hartmann, J., *Z. wiss. Phot.*, **1**, 259 (1903).

¹⁴¹ Luther, R., and Forbes, G. S., *J. Am. Chem. Soc.*, **31**, 770 (1909).

¹⁴² Winther, C., *Z. Elektrochem.*, **19**, 389 (1913), for filters for other lines, (5790, 5460, 4360, 4050, and 3130A), see Winther, C., *Ibid.*, **43**, 691 (1937).

¹⁴³ Andrich, K., and Le Blanc, M., *Z. wiss. Phot.*, **15**, 187 (1915).

¹⁴⁴ Buttolph, L. J., *J. Opt. Soc. Am.*, **6**, 1066 (1922).

¹⁴⁵ Gray, L. T. M., *J. Phys. Chem.*, **31**, 1732 (1927).

¹⁴⁶ Potapenko, G., *Z. wiss. Phot.*, **18**, 238; *Chem. Abs.*, **14**, 699 (1920).

¹⁴⁷ Miethe, A., and Stenger, E., *Z. wiss. Phot.*, **19**, 57 (1919); *J. Soc. Chem. Ind.*, **39**, 313A (1920).

¹⁴⁸ Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).

¹⁴⁹ Staats, E. M., *J. Opt. Soc. Am.*, **28**, 112 (1938).

receivers, they apply only to a specified source (H-3 capillary high-pressure mercury arc) and specified receivers.

When it is desired to remove infrared rays to prevent their possible effects on the temperature of solutions undergoing photochemical reactions, water is employed as a filter in a quartz cell. A 1-cm. thickness transmits 58 per cent at 9450A and 14 per cent at 11,900A.¹⁵⁰ Coblentz has suggested filters to absorb the infrared completely.¹⁵¹ Sodium, potassium, ammonium and thallium chlorides act as selective filters in the region 40-140 μ .¹⁵² A filter solution which transmits the visible rays and absorbs ultraviolet rays shorter than about 4000A may be made from quinine sulfate.¹⁵³ Clarke¹⁵⁴ describes a light filter for absorbing blue-violet and ultraviolet rays. It is formed of gelatin or other light-transmitting material containing a salt of glucose-phenylosazone-*p,p'*-dicarboxylic acid. An acid which in 0.01 per cent solution (2-cm. layer) absorbs ultraviolet and passes most of the visible rays is made by Suzuki and Sakurai¹⁵⁵ by condensing dextrose or invert sugar with phenylhydrazine-*p*-sulfonic acid in the presence of sodium or potassium acetate at 100°C. Used in a gelatin filter, 2 gms. per sq. meter, this filter completely absorbs the ultraviolet. It is claimed that the insoluble basic lead salt of the acid provides an ultraviolet-ray proof paint. A colorless pyrene compound, such as pyrene-3,5,8,10-tetrasulfonic acid, with steep absorption curve at about 4100A, has been proposed as a filter ingredient for removing ultraviolet rays by Wiegand, Merkel and Tietze.¹⁵⁶ Wilmanns, Dieterle and Weichmann¹⁵⁷ suggest for this purpose cyanines containing two benzoxazole rings, or one such ring and one benzothiazole ring, or a benzoxazole and a thiazoline ring, or a benzothiazole and thiazoline ring, bound in the 2,2'-positions to the nitrogen atom by a carbon atom.

Bakelite panels 0.5 mm. thick transmit 30 per cent at 3126A, 3 per cent at 2800A, and none at 2750A, the resin turning yellow.¹⁵⁸ Zernik¹⁵⁹ proposes hydroxylquinoline sulfonic acids and their alkyl or aryl ethers as colorless light filters for ultraviolet rays.

A filter for wave-lengths between 2900 and 3200A may comprise a film of trihydroxytriethylamine salicylate or *o*-cresotate or other compound of the formula HO—R—COONH(C₆H₄OH)₃, where R is a benzene or naphthalene ring and the hydroxyl group of the nucleus and the carboxyl group are in ortho-relation.¹⁶⁰

A series of long-wave-pass filters has been described by Schneider and Sperti.¹⁶¹ The shortest mercury arc line which appears on a photospectrogram through 2 cm. of each filter solution following an exposure of 5 seconds (Gaertner quartz spectrograph) is given in Table 16. The line of next shorter wave-length in each case does not appear with an exposure of 60 seconds. The figures given in the second

¹⁵⁰ Nichols, E. F., *Phys. Rev.*, **1**, 13 (1893).

¹⁵¹ Coblentz, W. W., *Bur. Standards Bull.*, **7**, 655 (1911); **9**, 110 (1913).

¹⁵² Hirsekorn, H. G., *Ann. Physik*, **6**, 985 (1930).

¹⁵³ Weyl, Th., "Die Methoden der Organischen Chemie," Vol. 1, p. 313, Leipzig, G. Thieme, (1909).

¹⁵⁴ Clarke, H. T., U. S. P. 1,293,039, Feb. 4, 1919.

¹⁵⁵ Suzuki, T., and Sakurai, S., U. S. P. 1,684,562, Sept. 18, 1932, to Zaidan Hojin Rikagaku Kenkyujo; *Chem. Abs.*, **22**, 4735 (1928). British P. 242,721, Aug. 18, 1924.

¹⁵⁶ Wiegand, C., Merkel, E., and Tietze, E., U. S. P. 2,122,828, July 5, 1938, *Chem. Abs.*, **32**, 6509 (1938).

¹⁵⁷ Wilmanns, G., Dieterle, W., and Weichmann, H. K., German P. 654,900, Jan. 4, 1938; *Chem. Abs.*, **32**, 3268 (1938).

¹⁵⁸ Risler, J., *Compt. rend.*, **181**, 782 (1925).

¹⁵⁹ Zernik, F., U. S. P. 1,688,259, Oct. 16, 1928; *Brit. Chem. Abs.*, **B**, 528 (1929).

¹⁶⁰ Stockelbach, F. E., U. S. P. 2,128,334, Aug. 30, 1938; *Chem. Abs.*, **32**, 8274 (1938).

¹⁶¹ Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 9 (1926); Goode, G. P., *Ibid.*, **5**, 41 (1933).

column are the number of cubic centimeters of water in which one gram of substance is dissolved.

Table 16.—Transmission of Ultraviolet Rays by Filters.

Salt	Dilution	Wave-length Limit, Å
Ammonium Sulfate	Concentrated	2030
Strontium Chloride	Concentrated	2120
Calcium Chloride	2	2220
Acetic Acid	500	2250
	50	2300
	20	2370
Lead Acetate	(0.28 g. per l.)	2380
	1000	2450
	600	2480
	200	2570
Copper Sulfate	100	2570
Lead Acetate	(15 g. per l.)	2650
	40	2680
	20	2750
Copper Sulfate	40	2880
	25	2960
	3	3130
Cupric Chloride	20	3340

In the preparation of these filters, no attention was paid to the purity or hydration of the materials. Instead, after preparation, the filters were tested spectrographically and adjusted by the addition of water or concentrated salt solution. A semi-commercial scale apparatus in which these filters may be employed for the irradiation of large areas of solutions or liquids of various kinds has been described. (Figure 91).¹⁶²

Two Hanovia 500-watt quartz mercury arc burners, operated at 135-145 volts a.c. are housed in two separate square metal shields equipped with air-cooling louvres. On the housing of each burner are mounted three filter cells, the frames of which are of chromium-plated brass, 10 by 17.5 cm., equipped with large quartz filter plates 2 cm. apart. The quartz plates are sealed to the cell frames with picein wax. The joints on the side next to the lamp are cooled by water which flows through the hollow section of the filter frame. The filter solutions are kept in five-gallon glass storage bottles in the top of the unit. All piping and valves in the filter feed and drain lines are either copper, brass, or chromium-plated brass. The filter solutions are forced through the lines by air pressure, maintained at ten pounds by a regulator. The flow is made visible by a drip cup in the drain line mounted on the front of the unit; its rate is adjusted to change the solution in each cell every fifteen minutes. Six different filter solutions and distilled water are available for each lamp at any time by opening the proper line valves on the front panel. Nitrogen and ice water outlets are mounted on the unit so that a nitrogen atmosphere and cooling may be applied continuously to the material irradiated. Motor-driven rotating and stirring devices are built into each lamp housing. It is possible to irradiate oils in thin films in large rotating cylinders, solutions in rotating test tubes, and liquids in various types of cells equipped with stirrers. The distance from the burners to the cells is approximately 15 cm. Three experiments, utilizing different filters, may be carried on simultaneously with each lamp, or six with the complete unit.

Withrow¹⁶³ describes filters for the region 2900 to 3200Å, made of solutions of organic acids adsorbed on regenerated cellulose or impregnated in gelatin sheets, the latter being the stronger and having the smoother surfaces. In each of the

¹⁶² Goode, G. P., *Bull. Basic Sci. Research*, 5, 39 (1933); U. S. P. 1,966,546-7, July 17, 1934, to General Development Laboratories, Inc.

¹⁶³ Withrow, R., *Bull. Basic Sci. Research*, 3, 82 (1931); U. S. P. 1,938,734, Dec. 12, 1933, to General Development Laboratories, Inc.

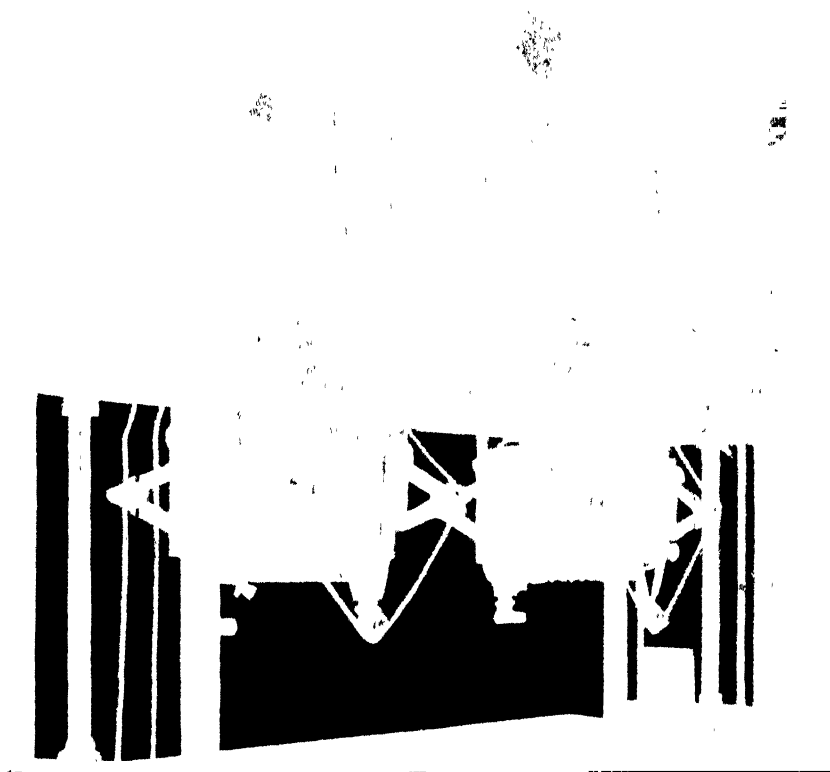


FIGURE 91. Ultraviolet Irradiation Unit. (Goode, *Bulletin Basic Science Research*).

three solutions used, the solvent is one liter of water and 125 cc. of glycerin to prevent cracking. No. 1 contains 80 gm. of sodium benzoate, No. 2, 40 gm. of potassium acid phthalate¹⁶⁴ and No. 3, 30 gm. of cinnamic acid and 10 gm. of potassium hydroxide. Sheets of the desired size of No. 600 Du Pont Cellophane are soaked in the desired solution for 12 hours and allowed to dry. In making gelatin filters, powdered gelatin in unspecified quantity is dissolved in the filter solution and the liquid spread on sheets of glass or quartz. The transmission curves of these three filters are given in Figure 92, in which Corex D and Quartz-lite are added for comparison. On intense irradiation, particularly with the shorter wave-lengths, these filters deteriorate, the absorption limit shifting toward longer wave-lengths. For this reason, it is advisable to use these filters in conjunction with a filter of Corex D which absorbs much of the energy in the shorter wave-lengths,

¹⁶⁴ Suggested by Saunders, F., *J. Opt. Soc. Am.*, 16, 362 (1928).

the gelatin filters serving to sharpen the absorption limits. Under such conditions, two sheets of No. 1, absorb practically all radiations shorter than the 2890A line, two sheets of No. 2 all beyond the 3130A line and three sheets of No. 3 those beyond the 3340A line.

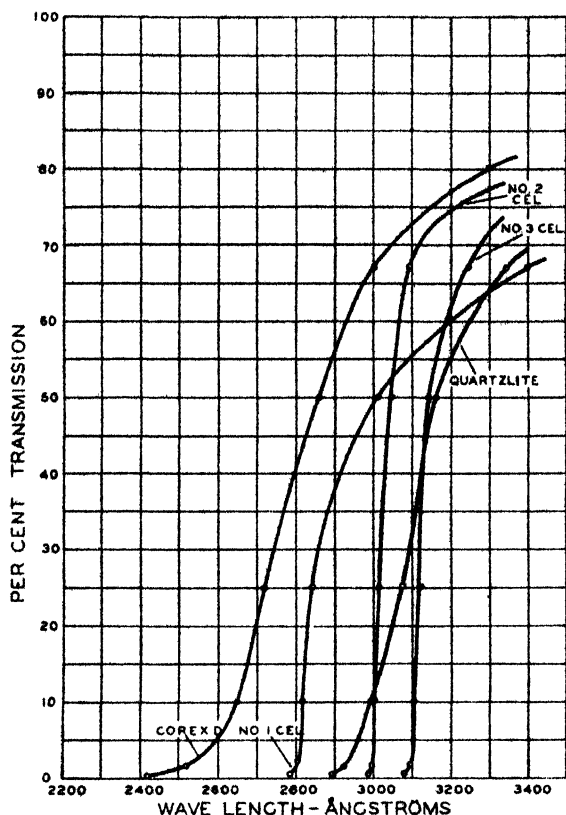


FIGURE 92. Transmission Characteristics of Various Filters (Withrow, *Bull. Basic Science Research*).

Jones¹⁸⁵ described a set of eight filters, only two of which were intended for the ultraviolet region, the others covering the visible and infrared. One ultraviolet filter was made by combining 2 cm. of 10 per cent copper sulfate solution with 3.2 mm. of Corning glass G 586. This filter transmits between 3300 and 4300A with a maximum of 69 per cent at 3800A. At all wave-lengths between 4300 and 12,000A, transmission is less than 0.1 per cent. The other ultraviolet filter combined a 1 cm. layer of a 50 per cent aqueous solution of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ with 3.2 mm. of Corning glass G 986A. It transmits between 2600 and 3600A, with a maximum of 50 per cent at 3100A. By adding 1 cm. of 2 per cent $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, all wave-lengths shorter than 3100A can be absorbed. Bhagwat¹⁸⁶ has determined the transmission of solu-

¹⁸⁵ Jones, L. A., *J. Opt. Soc. Am.*, 16, 259 (1928); *J. Nutrition*, 2, 111 (1929); *Chem. Abs.*, 24, 1889 (1930).

¹⁸⁶ Bhagwat, W. V., *J. Indian Chem. Soc.*, 11, 5 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh*, 2, 68 (1932); *Chem. Abs.*, 29, 7192 (1935).

tions of nickel salts. Combinations of these salts with cobalt salts transmit only in the ultraviolet, a mixture of 3.66*M* cobalt chloride and 2.08*M* nickel nitrate transmitting 3307-3598Å. The cobalt salt alone transmits the 2618-4063 and 7100-7600Å regions.

Another list of ultraviolet filters for the mercury lamp, most of which also remove the infrared, has been proposed by Bowen,¹⁸⁷ who employs the filters in round flasks which serve as condensers, increasing the light intensity. One flask a few centimeters from the lamp gives approximately parallel light. Two flasks almost in contact and with one nearly touching the burner, give more intense light converging to an image about 5 cm. beyond the second flask. For the regions (a) the yellow and green lines and (b) blue, violet and 3665Å lines, the first flask (glass, 10-12 cm. diameter) contains distilled water and the second, a double-walled Dewar flask, has the inner part filled with water and the 1-cm. space filled with a solution of 60 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 2 gm. $\text{K}_2\text{Cr}_2\text{O}_7$, 55 cc. of concentrated sulfuric acid and made up to one liter with water. With this arrangement, 3.4 mm. Corning 344 transmits only the 5790 and 5770Å lines, and 5 mm. Corning 512 only the green line 5460Å. For the region (b), the solution for the outer part of the Dewar flask is 20 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 300 cc. aqueous ammonia made to one liter with water. With this solution, 2.5 mm. Corning Noviol A glass transmits only the blue line 4360Å, 2 mm. of Corning Noviol 0 and 1 cm. of a carbon tetrachloride solution of iodine (7.5 gm. per liter) transmits only the 4060Å line and 2 to 2.5 mm. of Chance's black ultraviolet glass transmits only the line 3665Å.

For the ultraviolet region, 10 cm. spherical quartz flasks are used. For the region 3340-2800Å, the first flask has a solution of 70 gm. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 30 cc. concentrated hydrochloric acid per liter. For the region 2800-2480Å, a solution of one-fifth that concentration is employed. These solutions remove the infrared and 4060Å lines and greatly reduce the 3665Å line. For the 3340Å line, the second flask contains uric acid in water saturated at 15°C. For the 3135Å line, this flask has a potassium chromate solution made by diluting 5 cc. of a stock solution (3.0 gm. per liter) with 5 cc. of 2*N* sodium hydroxide and 490 cc. of water. The filter is used with a 1-cm. plane quartz cell containing circulated potassium hydrogen phthalate (13 gm. per liter) in water. For the 3135, 3030 and 2970Å lines, the second flask contains 60 cc. of a stock solution of Auramine 0 (0.125 gm. per liter) in 440 cc. of water, and is used with 1 cm. of circulating saturated benzoic acid in water. For the 3030 lines (and all shorter ones), the second flask contains water. For the 3030Å line, there is used 1 cm. of benzene circulating at the rate of 4 liters per hour; for 2650Å, chlorine gas at 760 mm. (3 cm. layer) and a circulating solution of pure benzene in water (1 cm.) (82 cc. of the saturated solution at 15°C. diluted to 100cc.). For the 2750-2480Å lines, 3 cm. of chlorine gas at atmospheric pressure is used. For the 2540Å line, there is employed in addition to the chlorine filter, 1 cm. of a solution made by diluting 8.6 cc. of a solution of 12.7 gm. iodine and 18 gm. of potassium iodide per liter, to one liter. Transmission data for these filter arrangements are given. Some changes in the list were made subsequently.¹⁸⁸

Slightly different filters, employing also cobalt sulfate in sodium cinnamate, have been recommended by Bäckström¹⁸⁹ for the medium ultraviolet region. Another series, using cobalt, chromium, copper, manganese and nickel salts has

¹⁸⁷ Bowen, E. J., *J. Chem. Soc.*, 2236 (1932).

¹⁸⁸ Bowen, E. J., *J. Chem. Soc.*, 76 (1935).

¹⁸⁹ Bäckström, H., *Naturwiss.*, 21, 251 (1933).

been described by Maddock¹⁷⁰ for isolating nine of the principal bands of the mercury spectrum from 2652 to 5780A, giving transmissions of 7 to 36 per cent. Still others are due to Vaidya,¹⁷¹ who describes 33 such systems and gives approximate measurements of the energy transmitted by eight of them.

For isolating for Raman studies the mercury triplet at 4358A, Sannié, Amy and Poremski¹⁷² use a filter solution containing 5 per cent nitrobenzene and 0.01 per cent rhodamine 5G Extra in ethanol. A thickness of 1 cm. gives a transmission of 0.001 for the lines 4046 and 4916 and of 0.95 for the desired triplet. Glass filters for other lines for Raman work have also been described by Amy.¹⁷³

In Raman work, the 4046A line is better absorbed by Noviol A than by sodium nitrite solution, which is subject to change.¹⁷⁴

According to Bhagwat and Dhar¹⁷⁵ the ammonia complex of cupric chloride is a good filter for the region 4000 to 4590A. Cupric chloride with cobaltous chloride is satisfactory for the lines 2961 and 3248-74A.

Mica¹⁷⁶ has occasionally been used as a filter material. Ruby mica absorbs the least; in a 0.03 mm. layer the transparency limit is 2900A. In 0.75 mm., it is 3500A. Green species absorb more strongly, as only traces pass through 0.5 mm. layers. Deep-brown Madagascar mica absorbs totally in 0.1 mm. layers.¹⁷⁷

Transmission by Clothing. It is of interest to consider the degree to which our clothing prevents access of the ultraviolet to the body. Dozier and Morgan¹⁷⁸ were unable to produce vitamin D in oils by irradiating them through baby flannel, pongee and crepe de Chine, although artificial silk and meadow lane materials transmitted the active rays. The mean interspace between threads and the weight are the important factors.¹⁷⁹ Trotman,¹⁸⁰ who used a light sensitive dyestuff as an indicator of the permeability of the fabric to ultraviolet, was unable to detect any transmission even through viscose, cuprammonium, chardonnnet and celanese rayons. Coblenz, Stair and Schoffstall¹⁸¹ have made physical measurements of the transmission of ultraviolet radiation through various fabrics. Comparing materials having the same weight, practically no difference was found in the amount transmitted through bleached samples of cotton, linen, viscose silk and cellulose acetate silk. Fresh, white natural silk is almost as translucent as bleached cotton, but wool is only half as transparent. In all cases when the fabric is dyed, or slightly yellow with age, the ultraviolet transmission through the thread is greatly decreased. Hence, in comparing dyed fabrics, the one with the largest openings between the threads transmits the most ultraviolet radiation.

Hirst, King and Lambert¹⁸² found every one of over a hundred fabrics to cut off a large proportion of the ultraviolet radiation, the weave and texture being more important than the material of the fiber. For equal thicknesses of material,

¹⁷⁰ Maddock, A. J., *J. Sci. Instruments*, **12**, 218 (1935).

¹⁷¹ Vaidya, B. K., *J. Univ. Bombay*, **3**, Pt. 2, 141 (1934); *Chem. Abs.*, **29**, 6508 (1935).

¹⁷² Sannié, C., Amy, L., and Poremski, V., *Compt. rend.*, **202**, 1042 (1936).

¹⁷³ Amy, L., *Documentat. Sci.*, **4**, 97 (1935); *Chem. Zentr.*, **II**, 2848 (1935).

¹⁷⁴ Biquard, D., *Documentat. Sci.*, **5**, 81 (1936); *Chem. Abs.*, **31**, 7758 (1937). See, however, Bayley, P. L., *J. Opt. Soc. Am.*, **27**, 303 (1937).

¹⁷⁵ Bhagwat, W. V., and Dhar, N. R., *J. Phys. Chem.*, **35**, 2383, 2391, 2401 (1931).

¹⁷⁶ Hausmann, W., and Krumpell, O., *Strahlentherapie*, **35**, 387 (1930); Takagi, T., *Ibid.*, **40**, 189 (1931).

¹⁷⁷ Finkelburg, W., *Naturwiss.*, **14**, 919 (1926).

¹⁷⁸ Dozier, C. C., and Morgan, H., *Am. J. Physiol.*, **84**, 603 (1928).

¹⁷⁹ Morgan, H., *Am. J. Physiol.*, **86**, 32 (1928).

¹⁸⁰ Trotman, S. R., *Textile Recorder*, **47**, 63 (1929); *Chem. Abs.*, **23**, 2297 (1929).

¹⁸¹ Coblenz, W. W., Stair, R., and Schoffstall, C. W., *Bur. Standards J. Research*, **1**, 105 (1928).

¹⁸² Hirst, H. R., King, P. E., and Lambert, P. N., *J. Soc. Dyers Colourists*, **44**, 109 (1928); *Chem. Abs.*, **22**, 2061 (1928); Eccles, J., *Silk J.*, **7**, 37 (1931).

they believed wool to have on the whole a higher transmissive power than the other fabrics tested. Any kind of dyeing decreases the ultraviolet transmission.

Young¹⁸³ suggested tracing cloth as a substitute for the more expensive ultraviolet glasses for use in country cottages, chicken farms, etc. This could not be confirmed at the Bureau of Standards. The total ultraviolet of wavelengths 2500-3100 diffusely transmitted through a new sample of tracing cloth amounted to about 26 per cent before wetting and 14 per cent after removing the sizing and drying the cloth. Balloon fabric transmits 21, batiste 16, and nainsook 31 per cent.

PHYSICAL METHODS FOR ISOLATING LINES OR WAVE-LENGTH BANDS

Unique among filters employing physical principles is that of Christiansen, which acts on¹⁸⁴ the principle that a suspension of a finely divided solid in a liquid transmits only radiations of the wave-length at which the refractive index of the solid is the same as that of the liquid. While such filters have frequently been used in the visible region, the principle has only recently been extended to the ultraviolet.¹⁸⁵ A solution of 56 per cent benzene and 44 per cent ethanol containing amorphous silica at 20°C. transmits at 3600Å. Such filters are very sensitive to temperature changes. Andrews¹⁸⁶ furnishes details of an apparatus for separating visible from ultraviolet light, which depends upon the fact that the visible rays are less refracted by a lens than is the ultraviolet radiation. Figure 93 diagrammatically shows the design of the apparatus. A is a source of visible

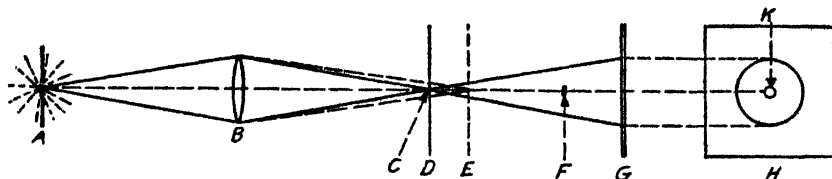


FIGURE 93. Diagram Showing Principle of Andrew's Separator.

light, also producing ultraviolet rays. B is a quartz lens. D is a thin sheet of metal pierced with a pinhole at C, the diaphragm being so placed that the pinhole is in the exact mean focus of the visible rays. F is a small metal disk and G is a screen. A front view of the screen is shown at H. The operation of this instrument is based on the fact that the mean focus of the visible light is located at a measurable distance beyond the mean focus of the invisible rays owing to the greater refrangibility of the latter over that of the former. If, therefore, the diaphragm D is carefully adjusted so as to bring the pinhole C into the exact mean focus of the ultraviolet rays, the rays of the latter will pass through the pinhole and spread out again on the other side of the diaphragm. The mean focus of the visible light being some distance beyond the pinhole, its rays will be largely intercepted by the diaphragm, and through the pinhole only a few of the nearly parallel rays of visible light will pass. In operation, if the screen H is made of non-fluorescent material, there will appear on it only the small illumi-

¹⁸³ Young, C. H., *Nature*, 123, 47 (1929).

¹⁸⁴ See Holst, G., *Z. wiss. Phot.*, 36, 145 (1937); *Brit. Chem. Abs.*, B, 479 (1937).

¹⁸⁵ Kohn, H., and v. Fragstein, K., *Physik. Z.*, 33, 929 (1932); Ahier, G., *Compt. rend.*, 205, 37 (1937).

¹⁸⁶ Andrews, W. S., *Gen. Electric Review*, 817 (1917).

nated spot K, but if it be coated with a fluorescent substance, such as powdered willemite, this small luminous spot will be surrounded by a disk of bright green light produced by the fluorescence of the willemite excited by the circular field of invisible ultraviolet rays. Should it be found desirable to cut out the spot of visible light, the small metal disk F can be set up in such a position as to cast its shadow over the spot K and so transform it from a bright spot to a dark one, leaving the disk of green fluorescent light otherwise unchanged.

The method has been extended by Terenin¹⁸⁷ to the separation of various ultraviolet regions. Forbes, Heidt and Spooner¹⁸⁸ prefer it to the monochromator for the aluminum lines around 1940A and the zinc lines near 2030-2014A.

Another way of getting a monochromatic radiation is to employ the rays given out by cold mercury vapor when transversely illuminated by a mercury vapor arc. This radiation is about one-fortieth as intense as the 2537A line of the original source, but offers some possibilities for photochemical work.¹⁸⁹ Very low voltage arcs also deliver monochromatic radiation in the resonance lines, but this radiation is of low intensity.¹⁹⁰

By far the most generally used optical method employs a prism monochromator. Light from the source passes through a slit to a prism (a collimating lens may be added) and after passing a lens emerges through an exit slit, which is narrow enough to exclude all but the desired wave-length region. This slit is also movable so that any desired wave-length range may be isolated. Any such instrument must, however, represent a compromise between monochromatic purity and loss of intensity. For greater intensities, monochromators are best employed with the constricted mercury arc as source. Details are to be found in the catalogs of instrument makers or in textbooks on optical instruments. Many photochemists design and build their own monochromators; valuable suggestions regarding such instruments and the optical losses they involve have been given by Forbes.¹⁹¹ Details have been given by Heidt and Daniels¹⁹² regarding laboratory-built instruments and by Kurtz¹⁹³ regarding a commercial type. Reflection losses in the Hilger monochromator have been studied by Ridyard and Style.¹⁹⁴ Granath¹⁹⁵ calculates that in the Hilger E 31 quartz spectrograph, the absorption at 1860A by the quartz is 50 per cent and by the air 17 per cent. At 1900A, the values are 31 per cent and 3 per cent, at 2000A, 23 per cent and 1 per cent and at 2100A, 16 per cent and 0.5 per cent, respectively. Forsythe and Barnes¹⁹⁶ have described a quartz monochromator especially intended for studying the intensity of the radiation in the ultraviolet spectrum from various sources.¹⁹⁷

¹⁸⁷ Terenin, A., *Z. Physik*, **31**, 33 (1925).

¹⁸⁸ Forbes, G. S., Heidt, L. J., and Spooner, L. W., *Rev. Sci. Instruments*, **5**, 253 (1934).

¹⁸⁹ Wood, R. W., *Physik. Z.*, **13**, 353 (1912); Cario, G., and Franck, J., *Z. Physik*, **17**, 205 (1923).

¹⁹⁰ Foote, P. D., and Meggers, W. F., *Bur. Standards Bull.*, **16**, 317 (1920).

¹⁹¹ Forbes, G. S., *J. Phys. Chem.*, **32**, 496 (1928).

¹⁹² Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, **54**, 2384 (1932); see also Benford, F., *J. Opt. Soc. Am.*, **26**, 99 (1936).

¹⁹³ Kurtz, H. F., *J. Opt. Soc. Am.*, **13**, 495 (1926); see also Villars, D. S., *J. Am. Chem. Soc.*, **49**, 326 (1927).

¹⁹⁴ Ridyard, H. N., and Style, D. W. G., *J. Phys. Chem.*, **32**, 861 (1928).

¹⁹⁵ Granath, L. P., *Phys. Rev.*, **34**, 1045 (1929).

¹⁹⁶ Forsythe, W. E., and Barnes, B. T., *Rev. Sci. Instruments*, **1**, 569 (1930).

¹⁹⁷ See also Fortrat, R., *Rev. optique*, **16**, 386 (1937); Pelton, M. O., *J. Sci. Instruments*, **15**, 169 (1938); Perry, J. W., *Proc. Phys. Soc. (London)*, **50**, 265 (1938).

Chapter 11

The Sun as a Source of Ultraviolet Radiations

The discussion of filters in the preceding chapter paves the way for a consideration of the amount and quality of the ultraviolet energy available on the earth's surface, since a large portion of the energy emitted by the sun is absorbed in the earth's atmosphere. Only about 70 to 78 per cent of the sun's total radiant energy of all wave-lengths which strikes the upper atmosphere gets through to sea level when the sun is at the zenith and the air is free from dust and clouds.¹

Astrophysical evidence indicates that the past billion years is only a small fraction of the period since the sun began to shine. In the past billion years, it has emitted 1.20×10^{50} ergs of energy (3.79×10^{33} ergs per second times 10^7 seconds per year $\times 10^9$ years). This is more than three billion billion billion kilowatt-hours. Expressed per gram of the sun's mass (1.983×10^{33} grams), the radiation per year is 6.05×10^7 ergs (1.44 calories); in a billion years at this rate, the radiation has amounted to 6.05×10^{16} ergs per gram, a lower limit.

It is believed that the whole ball of the sun is composed of hot gases, increasing inward in temperature and density. We see only the surface layer of gases—only down to where the density is a thousandth part of an atmosphere. This visible skin—photosphere—contains only as much mass as would a layer of a few feet of atmospheric air around the sun, far too little to produce the intense energy radiation. This must, therefore, be produced below the photosphere and flow toward the surface, which itself has a temperature of about 6000°K .

Many suggestions have been made as to the nature of the processes producing this energy; most of those based upon processes experimentally familiar have been found quantitatively inadequate. Recently, astronomers such as Eddington, have adopted the principle of Einstein that mass is in some way equivalent to energy and have built upon this models to describe the solar, or more generally, stellar radiation processes.

This principle states that a loss of m units of mass corresponds to the liberation of mc^2 units of energy, where c is the velocity of light. This constitutional energy is 8.99×10^{20} ergs per gram, about 15,000 times the estimated radiation per gram of the sun's mass during the past billion years. The Einstein principle of the equivalence of energy and mass would imply that the sun is losing 4,660,000 tons as energy per second, the earth receiving four pounds and three ounces as energy per second.²

In Eddington's theory, the material throughout the sun is in the state of a nearly perfect gas, the density increasing toward the center at such a rate that at the center it is about 54 times the mean density (1.41 grams per cubic centi-

¹ Stewart, J. Q., [*J. Frank. Inst.*, 204, 438 (1927)] has given an interesting general account of the theories of the origin of stellar energy, from which much of the information in these paragraphs has been derived.

² Discussion by Eddington, A. S., *Nature*, 117, Supplement to May 1 (1926); see, however, Jeans, Sir J., *Nature*, 117, 689 (1926); Menzel, D. H., *Science*, 65, 431 (1927); Nernst, W., *J. Frank. Inst.*, 206, 135 (1928). See also, Landau, L., *Compt. rend. acad. sci. U.R.S.S.*, 17, 305 (1937); *Chem. Abs.*, 32, 2426 (1938).

meter). This would make the central density more than three times greater than that of platinum. The gas at the center of the model sun is assumed to be under a pressure of more than a billion atmospheres and at a temperature of nearly 40 million degrees K. At such temperatures, it is believed that the shells of electrons are torn off from the atoms, leaving them stripped so that the kernels which remain are small enough for the gas to behave as such despite its high density.

Although considerations such as these are highly speculative, they may serve to afford some conception of the nature of the problems involved.

In the spectra of the sun about 60 elements have been identified.³ Russell⁴ has surveyed and discussed the evidence regarding the relative abundance of the elements in the sun's atmosphere. Sodium, magnesium, silicon, potassium, calcium and iron form 95 per cent of the whole mass. Elements of even atomic numbers are ten times as abundant as those of odd atomic numbers. The metals from sodium to zinc are far more common than any others. Compounds are present only in small amounts, cyanogen being rarer than scandium. The presence of boron and phosphorus has been much discussed. The estimated temperature of the reversing layer is 5600° and the pressure at its base is 0.005 atmosphere. It appears to contain 60 parts of hydrogen (by volume), two of helium, two of oxygen, one part of metallic vapor and 0.8 of free electrons. The temperature of the sun spots is close to 4900° absolute.⁵

Effects of the Earth's Atmosphere on Solar Radiation. Most of the lines which have been studied in deriving information on solar radiation have been located in the infrared and visible regions. Only a small part of the ultraviolet adjacent to the visible has been included. This is because the earth's atmosphere absorbs the shorter ultraviolet radiations; according to Lyman, the physicist Cornu found the spectrum of the sun to terminate quite abruptly at about 3000A. Our knowledge of the actual ultraviolet output of the sun, or of the amount of ultraviolet energy which reaches the outer layers of the earth's atmosphere is, therefore, limited because of absorption of ultraviolet within the atmosphere. It has been necessary to depend upon indirect methods, such as a consideration of the nature of the absorbing substance or substances and their distribution in the atmosphere in drawing conclusions as to the probable amounts of ultraviolet reaching the outer atmosphere. The most extensive estimates of the energy distribution outside the atmosphere have been made by Abbot⁶ for the region 4000A, and by Fabry and Buisson for shorter wave-lengths.⁷ The way in which this energy distribution is computed is about as follows: A series of observations is made of the normal incident energy at various times throughout the day. At these different times the rays pass through different lengths (or masses) of atmosphere. A vertical path gives an "air mass" of one. For variations from the vertical, the "air mass" varies as the secant of the angle. By graphical methods, it is possible to obtain from a series of intensity observations with different "air masses" an extrapolated value for an "air mass" of zero which represents the sun's energy before it is filtered by the atmosphere. Thus at 3100A the transmission for "air mass" of 1 is 0.1, and for "air mass" of 2, 0.01 (8 A.M. or 4 P.M.) and at "air

³ St. John, C. E., *Proc. Nat. Acad. Sci.*, 15, 789 (1929); *Astrophys. J.*, 70, 160 (1930); Dingle, H., in article "Sun" in *Encyclopedia Britannica*, 14th ed.

⁴ Russell, H. N., *Astrophys. J.*, 70, 11 (1929).

⁵ Richardson, R. S., *Astrophys. J.*, 73, 216 (1931).

⁶ Abbot, C. G., *Smithsonian Miscellaneous Collections*, 74, 15 (1923); *Annals Astrophysical Observatory*, 2, 112 (1908).

⁷ Fabry, C., and Buisson, H., *Compt. rend.*, 175, 156 (1922); *Astrophys. J.*, 54, 297 (1921).

mass" of 3 it is only one part in a thousand.⁸ During the stratosphere flight of the Explorer II to 72,395 feet, the total ultraviolet increased not over 4 per cent.⁹

From the standpoint of the biologist, the absorption of radiations of the shorter ultraviolet rays by the atmosphere is of the greatest importance. It is shown in Chapter 35 that ultraviolet rays shorter than about 2950Å are lethal to bacteria and destructive to living cells. Life, as we know it, could not exist on the earth if the absorption of these shorter rays in the atmosphere did not occur.

It is, therefore, interesting to determine which component of the atmosphere absorbs these rays. Both oxygen and nitrogen absorb strongly only rays of very much shorter wave-length (1850Å and less than 1250Å, respectively). Accurate data on the absorption by oxygen in the region 1850 to 2300Å have been determined by Granath.¹⁰ Earlier important observations were due to Fabry and Buisson,¹¹ Ladenburg and Lehmann,¹² and Hallwachs.¹³ That the absorbing component for bactericidal radiations is ozone has been known for many years, Hartley having been credited with first suggesting it.¹⁴ The origin of ozone in the upper atmosphere is still, however, an unsolved problem, despite a considerable amount of work.¹⁵ According to Fabry,¹⁶ a thickness of ozone of about 3 mm. at normal temperature and pressure would account for the observed absorption. This was calculated from absorption measurements of known concentrations of ozone and of varying thicknesses of the absorbing layer of the earth's atmosphere. Subsequently, a number of papers have been devoted to the distribution of ozone in the atmosphere.

Probably the best opportunity for accurate studies was afforded by the stratosphere flights of the Explorers I and II. These indicated little ozone up to 52,000 feet. Above this, the concentration of ozone increased rather rapidly and at 72,000 feet nearly 25 per cent of the total quantity of ozone lay below the level of the balloon. In the summer flight of 1934, the ozone was equivalent to 2.5 mm. and in the November flight of 1935 to 1.9 mm.¹⁷

Nitric acid occurs in the atmosphere, more at high than at low altitudes.¹⁸ It has been suggested that the nitrates and nitrites present in the atmosphere are derived from the photochemical oxidation of ammonia.¹⁹ Vorländer and Gohdes²⁰ find moist air to contain oxides of nitrogen to the extent of $15\text{--}30 \times 10^{-6}$ gm. per

⁸ Gordon, N. T., and Benford, F., *Gen. Electric Review*, 33, 283 (1930).

⁹ Teele, R. P., *National Geographic Society, Stratosphere Series*, No. 2, 133 (1936).

¹⁰ Granath, L. P., *Phys. Rev.*, 34, 1045 (1929).

¹¹ Fabry, C., and Buisson, H., *Compt. rend.*, 156, 782 (1913).

¹² Ladenburg, E., and Lehmann, E., *Ber. deutsche physik. Ges.*, 4, 125 (1906).

¹³ Hallwachs, W., *Ann. Physik*, 30, 602 (1909).

¹⁴ Hartley, W. N., *J. Chem. Phys.*, 111 (1881), cited by O'Brien, B., *National Geographic Society, Stratosphere Series*, No. 2, 49 (1936). For recent observations, Dejean, G., and Arnulf, A., *Compt. rend.*, 205, 1000 (1937); Vassé, F., *Ann. phys.*, 8, 679 (1937).

¹⁵ Rayleigh, Lord, *Science*, 70, 83 (1929); Rosseland, S., *Nature*, 123, 761 (1929); Ångström, A., *Gerland's Beitr. z. Geophysik*, 21, 2, 145 (1922); Dobson, G. M. B., Harrison, D. N., and Lawrence, J., *Proc. Roy. Soc.*, 114A, 521 (1927); Dauvillier, A., *Compt. rend.*, 197, 1339 (1933); Barbier, D., Chalonge, D., and Vassé, E., *Compt. rend.*, 201, 787 (1935); Fowle, F. E., *J. Terrestrial Magnetism and Atm. Elec.*, 33, 151 (1928); Dobson, G. M. B., Kimball, H., and Kidson, E., *Proc. Roy. Soc.*, 129A, 411 (1930); Wulf, O. R., *Phil. Mag.*, 17, 251 (1934); *J. Opt. Soc. Am.*, 25, 231 (1935); Harteck, P., *Naturwiss.*, 19, 858 (1931); Mecke, R., *Z. physik. Chem. Bodenstein Festschrift*, 329 (1931); Saha, M. N., *Proc. Roy. Soc. A*160, 155 (1937).

¹⁶ Fabry, C., *J. Math. Physics*, 4, 1 (1925); Cabannes, J., and Dufay, J., *J. Phys. Radium*, 7, 257 (1926).

¹⁷ O'Brien, B., *National Geographic Society, Stratosphere Series*, No. 2 (1936). Compare Regener, V. H., *Z. Physik*, 109, 642 (1938). A recent theoretical calculation of the vertical distribution of ozone is due to Wulf, O. R., and Deming, L. S., *Terr. Mag.*, 41, 299 (1936).

¹⁸ Rao, G. G., and Dhar, N. R., *Z. anorg. allgem. Chem.*, 199, 422 (1931).

¹⁹ Rao, G. G., *Bull. Acad. Sci., United Provinces Agra Oudh Allahabad, India*, 1, 82 (1931); *Chem. Abs.*, 26, 5849 (1932).

²⁰ Vorländer, D., and Gohdes, W., *Ber.*, 64B, 1776 (1931).

cubic meter of N_2O_8 . Irradiation with ultraviolet increases this from ten to a hundred times. Ammonia may be decomposed into nitrogen and hydrogen in the stratosphere.²¹ Formaldehyde may also be present in air since it may be detected in rainwater. The amount therein is not increased by lightning, but is greater when the rainfall has been preceded by some sunny days. Dhar and Ram²² suggest that formaldehyde may be produced from carbon dioxide and water by radiation of wave-length 2550A, at altitudes where this radiation has not all been absorbed by the ozone layer.

Suspended ultramicroscopic particles, partly consisting of ammonium nitrite and nitrate and sodium chloride and perchlorate, cause a scattering of radiations, greater at altitudes above those where rain exerts a cleansing effect. Duclaux²³ believes that this may play some part in causing the disappearance of the solar spectrum beyond the ozone bands, and that absorption by oxygen in the short wave region may not wholly account for it.

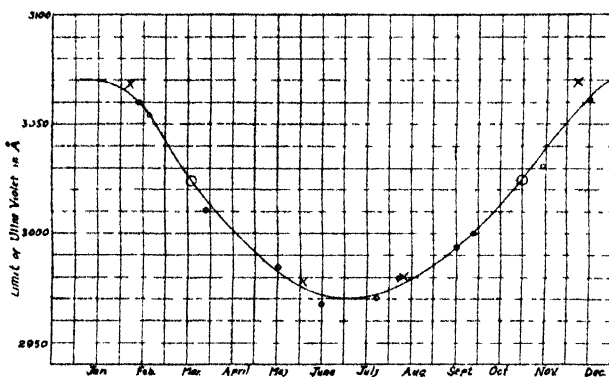


FIGURE 94. Prof. Winchester's Limit of Blackening on Photographic Plates for North Sky at New Brunswick (N. J.) for Different Seasons of the Year (Forsythe and Christison, *General Electric Review*). The vertical line above each month denotes its beginning. \circ = Winchester's values. \times = Points plotted from data in paper of Forsythe and Christison. \circ = Two calculated points.

Limits of the Solar Spectrum. Comparatively few workers have been interested in determining the long wave region at which solar radiation first penetrates to the earth. Adel, Slipher and Barker²⁴ place it at 13.5μ and attribute it mainly to vibration spectra of carbon dioxide and to a lesser extent to ozone. Beyond 17μ there is also absorption by water vapor, the effect of which is also observed in the red region of the visible, according to Beletskii.²⁵ The regions 8-9 and $10\text{--}12\mu$ have high transparency. This radiation in the remote infrared is, however, insignificant in amount; Coblentz and Kahler²⁶ have stated that but little radiation of wave-lengths greater than 2μ is transmitted by the earth's atmosphere. On some days the infrared energy component from about 2 to 3μ to the limit of the visible may be larger than the visible component. On clear days the two components may be about equal or the visible one may exceed the infrared.

²¹ Matignon, C., *Chimie et Industrie*, Special No. 328, September, 1925.

²² Dhar, N. R., and Ram, A., *Nature*, 132, 819 (1933).

²³ Duclaux, J., *J. phys. Radium*, 4, 625 (1933).

²⁴ Adel, A., Slipher, V. M., and Barker, E. F., *Phys. Rev.*, 47, 251, 580 (1935).

²⁵ Beletskii, F. A., *Zhur. Geofis.*, 6, 64 (1936); *Chem. Abs.*, 31, 3383 (1937).

There have been many determinations of the short-wave length limit since the time of Cornu, but his value of 3000A holds fairly well. The exact value varies greatly with seasonal, altitudinal and other influences. Coblenz and Kahler believed that radiations less than 3000A, if present, amount to less than 5 per cent (20 per cent in the mercury arc) of the total ultraviolet component. Others have stated the limit as 2900A or 2845A. Its variation at Davos in the Swiss Alps has been widely quoted.²⁷ From December to February, it was 3120A, September to November, 3080A, March to May, 3010A, June to August, 2962A.²⁸ Fabry and Buisson²⁹ showed that the amount of energy of wave-length 2900A that reaches the earth's surface is only one-millionth that for 3140A, and even for the larger value the intensity is small. Winchester has given an experimental curve (Figure 94) showing the wave-length limit at New Brunswick, N. J., as detected by the blackening of photographic plates exposed to the north sky at various times of the year. The shortest wave-length found was 2968A on June 1.³⁰

AMOUNTS AND DISTRIBUTION OF SOLAR ULTRAVIOLET

Coblenz and Kahler³¹ state that the maximum normal solar radiation at perpendicular incidence varies from 1.37 gram calories per minute per square centimeter in January at Washington to 1.5 in May and September. The average seasonal intensity for three hours at noon may be taken as 1.2 gram calories per square centimeter per minute. The total radiation on a horizontal surface, with a clear sky, varies from 0.77 gram calories per minute in December to 1.55 in June. Clouds nearly in line with the sun, but not obscuring it, increase the radiation by about 0.15 gram calories. Otherwise expressed, the maximum radiation that can be received normal to the incident energy is 106 milliwatts per square centimeter.³² Of the total radiation, only one or two per cent is in the ultraviolet with wave-lengths less than 3889A and more usually may be about half this, while in the case of the quartz mercury arc it may be 30 per cent. Coblenz and Stair³³ found that the upper limit of the total ultraviolet radiation of wave-lengths less than 3100A is less than 0.004 gram calories per square centimeter per minute at sea-level. It cannot exceed 0.3 per cent of the total incident radiation or approximately 300 microwatts per square centimeter. Recently, Coblenz believed this figure should be reduced to less than 100 microwatts per square centimeter.³⁴ Luckiesh³⁵ concludes that the best midsummer sunlight supplies not less than 25 microwatts per square centimeter, with a probable value of 40 microwatts per square centimeter, of ultraviolet energy shorter than 3100A.

With the growing appreciation of the rickets-preventing value of the radiations between about 3150 and 2900A, there have appeared a great number of studies of the intensity of the available energy in this region and its seasonal, meteorological, altitudinal and other variations.³⁶ Especial attention has been

²⁶ Coblenz, W. W., and Kahler, H., *Sci. Papers Bur. Standards*, No. 378 (1920).

²⁷ Dorno, C., *Strahlentherapie*, 31, 341 (1929); Kiepenhauer, K. O., *Naturwiss.*, 25, 669 (1937).

²⁸ Cited by Price, W. A., *Ind. Eng. Chem.*, 18, 679 (1926).

²⁹ Cited by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.*, 32, 664 (1929).

³⁰ Curve reproduced by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.*, 32, 667 (1929).

³¹ Coblenz, W. W., and Kahler, H., *Sci. Paper 378, U. S. Bureau of Standards*, 1920.

³² Gordon, N. T., and Benford, F., *Gen. Elec. Rev.*, 33, 283 (1930).

³³ Coblenz, W. W., and Stair, R., *Bureau Standards J. Res.*, 3, 629 (1929).

³⁴ Coblenz, W. W., *Trans. Illum. Eng. Soc.*, 26, 574 (1931).

³⁵ Luckiesh, M., "Artificial Sunlight," Van Nostrand, 1920, cited by Coblenz, W. W.; see also Forsythe, W. E., and Christison, F., *J. Opt. Soc. Am.*, 20, 396 (1930).

³⁶ Hill, G. L., *Proc. Roy. Soc.*, 102B, 119 (1927).

devoted to the effects of dust and smoke in lowering the biologically valuable rays.³⁷ Ashworth³⁸ considers the effects of winds from towns.

Forsythe and Christison³⁹ calculated from Abbot's data on the distribution of energy in solar radiations, curves of the transmission of the atmosphere for several wave-length regions, giving the per cents of total radiation and their amounts in milliwatts per square centimeter at Cleveland, Ohio for a horizontal surface, *i.e.*, corrected for the sun's distance from the zenith (Table 17). It must

Table 17.—Transmission of Ultraviolet Rays by Atmosphere.

Region	1 Atmosphere		1.07 Atmosphere June 21		1.5 Atmosphere Feb. 15		2.37 Atmosphere Dec. 21	
	%	Milliwatts	%	Milliwatts	%	Milliwatts	%	Milliwatts
0.31-0.29 μ	0.022	0.024	0.019	0.020	0.0063	0.0061	0.00051	0.0004
Below 0.325	0.24	0.26	0.21	0.22	0.11	0.11	0.029	0.023
Below 0.35	1.1	1.17	1.0	1.07	0.64	0.63	0.27	0.22
Below 0.40	3.9	4.22	3.8	3.97	2.8	2.70	1.62	1.3
0.40-0.76 μ	43.7	46.8	43.9	45.8	42.1	40.4	39.1	31.4
Total		107.0		104.5		96.1		80.2

be noted that these are calculated values, rather than the direct results of actual measurements. The values are in fair agreement with similar calculations by Holladay⁴⁰ based upon the assumption that the sun radiates as a black body at 6000°K. The paper of Forsythe and Christison also contains theoretical curves showing the variation of energy below 3250 and below 3100A per square centimeter at Cleveland at various times of day during the winter and summer solstices and the spring and fall equinoxes. There is also given a curve for the

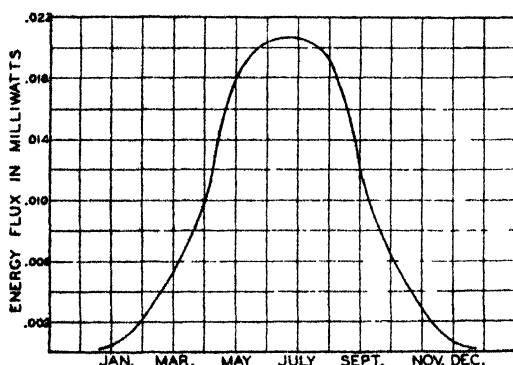


FIGURE 95.

Ultraviolet Energy Below 3100A from the Sun Falling upon a Square Centimeter of the Earth's Surface per Second for the Latitude of Cleveland, Ohio, at Different Times of the Year for 12 Noon. The vertical line above each month denotes its beginning (Forsythe and Christison, *General Electric Review*).

variation of intensity of wave-lengths less than 3100A at noon throughout the year at Cleveland (Figure 95). They concluded it doubtful if any energy in this region is received from the sun in winter at or near a city where the dust and smoke are quite thick. The making of intensity measurements at various wave-

³⁷ Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, **89**, 187 (1927).

³⁸ Ashworth, J. R., *Dept. Sci. Ind. Research, 20th Rept. Investigations of Air Pollution (England)*, 59 (1935); *Chem. Abs.*, **29**, 5560 (1935).

³⁹ Forsythe, W. F., and Christison, F., *Gen. Elec. Rev.*, **32**, 664 (1929); *J. Opt. Soc. Am.*, **20**, 401 (1930).

⁴⁰ Holladay, L. L., *J. Opt. Soc. Am.*, **17**, 329 (1928).

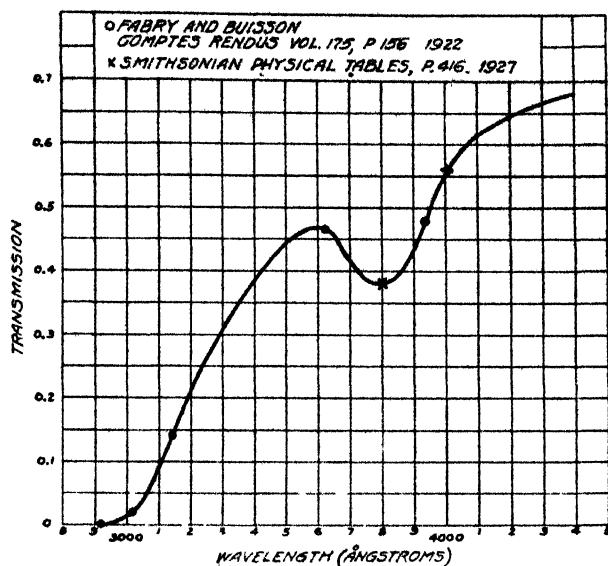


FIGURE 96. Transmission Factors of Earth's Atmosphere (Forsythe and Christison, *General Electric Review*).

lengths in the ultraviolet requires expensive equipment and skill, and comparatively few have made such measurements. In the region around 3000A, the data are of somewhat lower accuracy than in the visible region. There are irregularities when the data of Fabry and Buisson and of Abbot are combined in one curve for the transmission of the atmosphere. (Figure 96.) For this reason more direct determinations are desirable.

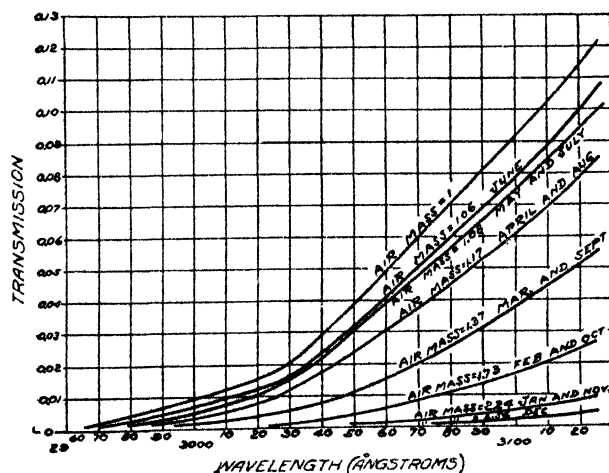


FIGURE 97. Transmission of Atmosphere for Erythema Radiation at Noon, Latitude of Schenectady, N. Y. (Gordon and Benford, *General Electric Review*).

Gordon and Benford⁴¹ give calculated curves (Figure 97) for the atmospheric transmission of radiations of wave-lengths 2900 to 3130A for the "air masses" corresponding to various times of the year. The data of Fabry and Buisson for air mass of 1 were employed, and the transmissions were calculated for the latitude of Schenectady. It is evident that the transmission of the biologically effective rays becomes almost negligible in December as compared with the values of June. These values are also based upon the assumption of cloudless skies, so that the actual values are much smaller in winter months when dark days prevail. These values neglect radiation reflected by clouds and scattered by the blue sky, and radiation received from the sky, which has been estimated to be from one

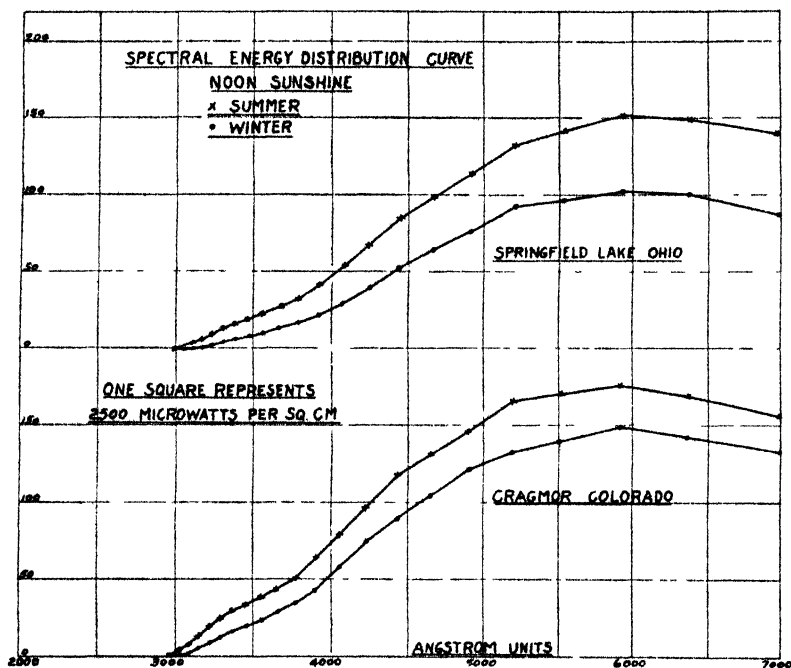


FIGURE 98. Energy Distribution Curve, Sunlight at Cragmor and Springfield Lake. (Greider and Downes, *Transactions Illuminating Engineering Society*).

quarter to three-quarters of the amount of direct radiation received from the sun. Regarding this, however, definite statements can scarcely be made. Coblenz,⁴² by using a thermocouple and diaphragms subtending an angle of 45 degrees of the sky, found in winter at Washington (low humidity) less than 7 per cent of ultraviolet sky radiation in the total directly incident ultraviolet measured. On a hazy day with high humidity, the ultraviolet sky radiation was 10 per cent of the total incident ultraviolet radiation from the sun. Pettit⁴³ studied the effect of

⁴¹ Gordon, N. T., and Benford, F., *Gen. Elec. Rev.*, 33, 283 (1930). For a recent theoretical treatment of data from the Smithsonian observatory at Montezuma, see Kiu, T., *J. phys. radium*, 9, 297 (1938).

⁴² Coblenz, W. W., *Trans. Illum. Eng. Soc.*, 26, 576 (1931).

⁴³ Pettit, E., *Trans. Nat. Tuberculosis Assn. 24th Ann. Meeting*, 110 (1928), cited by Coblenz, W. W.

Table 18.—Transmission of Ultraviolet Rays.

Noon sunshine intensities (watts $\times 10^{-7}$ per sq. mm.)

	Antirachitic ultraviolet 2900-3100A	Non-penetrating ultraviolet and visible 3100-6500A	Penetrating red and near infrared 6500-14,000A	Non-penetrating infrared 14,000-120,000A
Springfield Lake,				
October, 1928	1.2	2894	3660	1760
May-June, 1929	2.3	3404	3786	1834
December, 1929	0.49	2440	3720	1615
Cragmoor,				
November, 1928	1.6	3534	4432	1860
June, 1929	5.3	4233	4686	2211
January, 1930	1.1	3390	4565	1915
"Clinical sunlight"*	1.4	3214	4045	1810

* This is the preferred heliotherapy dosage in these institutions corresponding to early morning and late afternoon in summer and noon in winter.

atmospheric scattering. He found on a clear day at Pasadena that the intensity of the ultraviolet radiation from the sky was 11 units as compared with 22 units from the sun plus the sky or 50 per cent of the total. But at Mt. Wilson, the sky contributed only 30 per cent of the total (7 units out of 23.3).

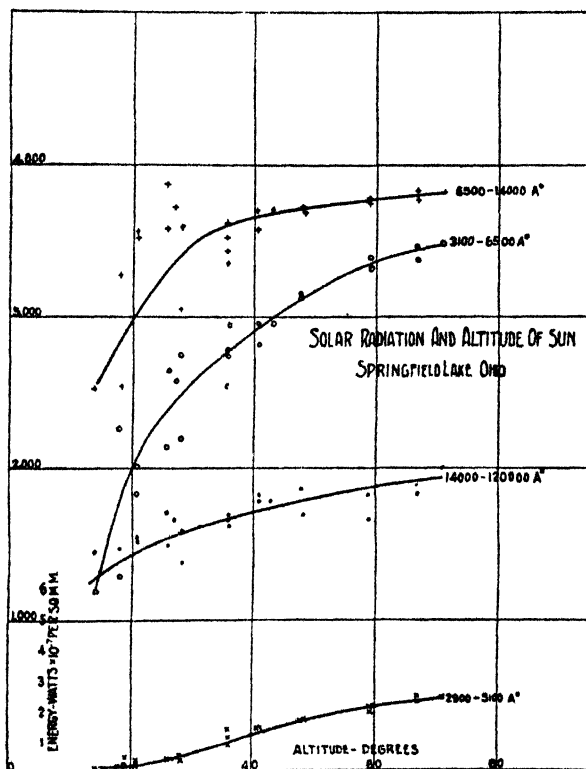


FIGURE 99. Solar Radiation and Altitude of the Sun, Springfield Lake, Ohio.
(Greider and Downes, *Transactions Illuminating Engineering Society*).

It is well known that the north sky is richer in ultraviolet than is direct sunlight, but ⁴⁴ the intensity of light falling in winter at noon on a north window is only about 300 foot-candles as compared with 1100 on a south window.

Greider and Downes ⁴⁵ reported direct energy measurements at Springfield Lake Sanatorium in Ohio (representative of low altitude locations in this latitude) and at Cragmoor Sanatorium in Colorado ("mountain sun"). Figure 98 shows the noonday values for winter and summer at these locations. The data are summarized in Table 18. Here it is apparent that the variation between summer and winter is less than one to five in the region 2900 to 3100A, which is far less than might be expected from the calculated curves of Gordon and Benford.

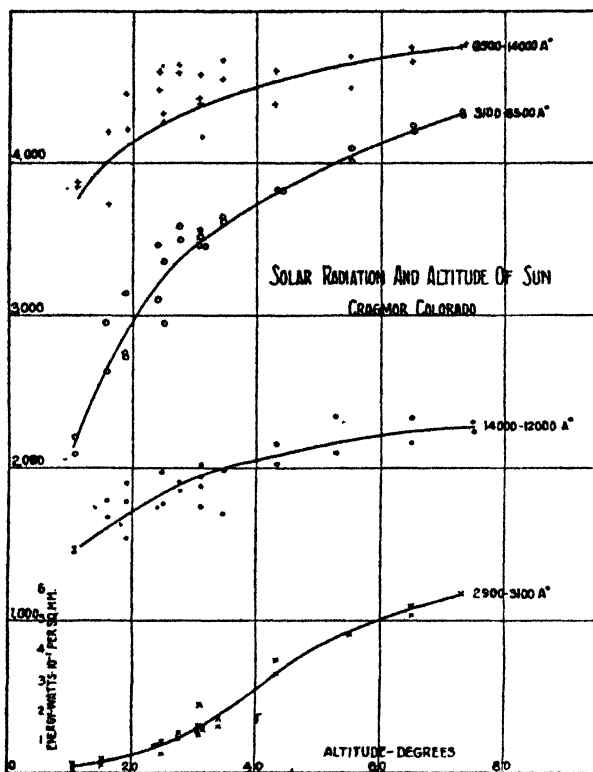


FIGURE 100. Solar Radiation and Altitude of Sun, Cragmoor, Colorado. (Greider and Downes, *Transactions Illuminating Engineering Society*).

Greider and Downes have also plotted (Figures 99 and 100), for the two locations, curves of the intensities within the wave-length regions of the table as affected by the altitude of the sun at various hours of the day. These curves can be used to determine the average intensity of the sun at any location at which the transmission of the air is similar to that at either of the locations studied. The

⁴⁴ Kimball, H. H., and Hand, I. F., *Monthly Weather Rev.*, **50**, 615 (1922), cited by Koblenz, W. W.

⁴⁵ Greider, C. E., and Downes, A. C., *Trans. Illum. Eng. Soc.*, **25**, 378 (1930); **26**, 561 (1931).

altitude of the sun is calculated for the location and time desired and the intensity may then be read from the curves. At the spring and fall equinox the altitude of the sun at noon is 90 degrees minus the latitude. At other times the value is increased or decreased by the amount of the sun's declination. For hours other than noon, the altitude is given by the equation

$$\sin h = \sin \phi \sin \delta + \cos \phi \cos \delta \cos t$$

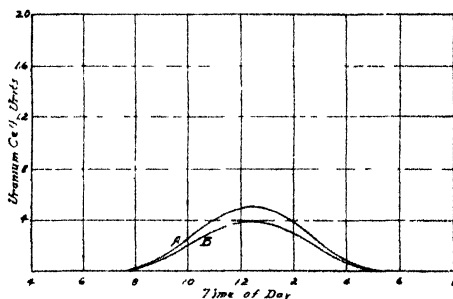
where h is the altitude of the sun, ϕ its declination, δ the latitude of the place of observation, and t the hour angle, which is approximately 15° for each hour before or after noon.

Such results can of course be only approximations, as they take no account of cloudiness, atmospheric pollution with dust or smoke, or the cleansing effect of rainfall. Coblenz⁴⁶ mentions the pronounced effect of dense low-lying strata of finely divided particles from automobile exhausts. The influence of a peak in automobile traffic can be detected in the amount of ultraviolet reaching the earth. Coblenz made photoelectric cell measurements, using a standard screen of barium flint glass. The component of radiation 3130 to 4000Å relative to the total ultraviolet 2900 to 4000Å measured in June sunlight at sea level was as follows: direct sunlight, 75 per cent; overcast sky during a light rain (the diaphragmed opening in front of the photoelectric cell subtended 18 degrees), 60 per cent; light overcast sky, 50 per cent; blue sky, 55 per cent; dark cloud, 64 per cent; within the laboratory, 4.5 meters from an open window, light from dark clouds through trees, 64-65 per cent. The difference between these values and 100 per cent is a measure of the component 2900 to 3130Å.

The Rentschler ultraviolet meter was employed by Meller, Hibben and Warga in a series of observations on the roof of a nine-story building in Pittsburgh. The cathode was mechanically rotated so as to be normal to the sun's rays. A Westinghouse watt-hour demand meter recorded the results; each line on the chart of the meter, representing the number of impulses in five minutes, is pro-

FIGURE 101.

Intensity of Ultraviolet Radiation for December 30, 1930. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).



portional in length to the amount of ultraviolet received at the photo-cell in that period. Records showing the comparative amounts of ultraviolet for an entire day were obtained in this manner. The intermittent obscuring effects of clouds or smoke were readily apparent. Slightly more ultraviolet was recorded on a day having scattered clouds than on a relatively clear day with slightly lower humidity. Even on a clear day there was a 100 per cent change in ultraviolet

⁴⁶ Coblenz, W. W., *Trans. Illum. Eng. Soc.*, 26, 572 (1931).

received in a period of 15 or 20 minutes. For comparison, the zinc sulfide and oxalic acid methods were also employed, but exact comparisons could not be made, as the amounts of sky exposure and the sensitivity curves differed in the methods as employed. Meller and Warga⁴⁷ studied the effects of air contaminants on the natural light of cities. Similar data were obtained by Kunerth and Miller⁴⁸ using the Rentschler meter without the aid of a graphical recorder at Ames, Iowa. Again the units are arbitrary, merely the number of impulses per second. The curves, Figures 101 and 102, show the ultraviolet in the sun and sky light and in

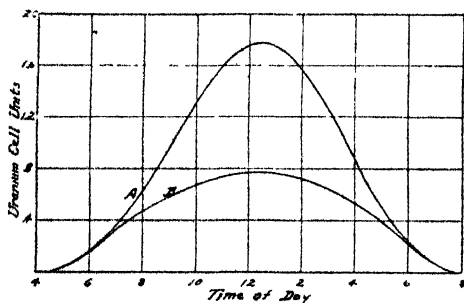


FIGURE 102.

Intensity of Ultraviolet Radiation for June 23, 1931. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

the latter alone during the course of days in December and June. The energy from the north half of the sky at noon is approximately equal to one-fifth of the total from sun and sky combined. The variation of sky and sun ultraviolet with altitude of the sun and with month of the year are given in tables. The presence of snow on the ground increases the ultraviolet from sun and sky by about 20 per cent. From the data obtained by the meter exposed to sources otherwise calibrated, it appeared that each impulse of the meter was equal to about 39,000 ergs or 3000 ergs per square centimeter. These authors also presented curves for the visible region from the sun and sky and from the latter alone. The total flux on a horizontal plane throughout the year at latitude 42°N if all days are clear is 16,820,000 lumen-hours per square foot, of which 11,870,000 are received in spring and summer and 4,950,000 in autumn and winter. At noon at the winter solstice, the light from the sky is approximately 16 per cent of the total; at the summer solstice, it is 10 per cent.

At New Orleans, the average daily amount of direct solar radiation of wavelengths less than 3130Å is less than 0.001 calorie per square centimeter from April to October and between 0.001 and 0.002 during the rest of the year. For the prevention of leg weakness in chickens, the amount required is about 0.00069 calorie per square centimeter daily.⁴⁹

⁴⁷ Meller, H. B., and Warga, M. E., *Am. J. Public Health*, 23, 217 (1933).

⁴⁸ Kunerth, W., and Miller, R. D., *Trans. Illum. Eng. Soc.*, 27, 88 (1932).

⁴⁹ Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, 102, 422 (1932).

Part II

Photochemical Processes

Chapter 12

Introduction to the Mechanism of Photochemical Processes

Among the earliest photochemical phenomena observed were the influence of light on the bleaching of linen, and the fading of certain natural dyes and pigments. The effect of light in developing the green color of plants, and the ability of green plants in some way to utilize the energy of the sun in converting carbon dioxide and water to carbohydrates and oxygen were recognized shortly after chemical knowledge had progressed to a stage at which the nature of combustion had become clear. A number of phosphorescent substances early attracted much attention. The photosensitivity of silver salts played an important part in the discovery of the existence of ultraviolet light. (Chapter 1.) The effect of light in accelerating the combination of hydrogen and chlorine, the decomposition of chlorine water, and the reduction of mercuric chloride solutions containing oxalic acid were the subject of a number of early papers.¹

Grotthuss, in 1817, in studying the fading of alcoholic solutions of ferric chloride and other iron salts, concluded that only light which is absorbed can act chemically. This rather obvious statement, now frequently called the first law of photochemistry, at first attracted little attention, as interest in the energy relations of chemical processes was not yet general. The Grotthuss law was independently rediscovered by Draper in 1843 in the course of investigations on the photochemical combination of hydrogen and chlorine.²

The first extensive kinetic studies of a photochemical reaction were those of Bunsen and Roscoe (1855-1862) upon the hydrogen-chlorine combination. (See Chapter 18.) The choice of this reaction was unfortunate, since it is very susceptible to the influence of traces of impurities, the presence of which gives rise to a latent period between the beginning of illumination and the start of the reaction. The observation of an induction period in a reaction so apparently simple led Bunsen and Roscoe and subsequent workers to attach undue importance to induction periods as a feature peculiar to photochemical changes. They did, however, succeed in showing that in general the amount of material transformed in a photochemical change is proportional to the product of the light intensity and the time of illumination. (Bunsen-Roscoe Law.)

Subsequently, a few other reactions were studied, including the oxidation of oxalic acid,³ the drying of oils, the decomposition of amyl nitrite,⁴ the polymerization of anthracene,⁵ and of vinyl halides.⁶ About 1900 the Italian investigator Ciamician began with Silber a series of researches in which the substances pro-

¹ For details of the history of early photochemical work, see Plotnikow, "Allgemeine Photochemie," 2nd ed., 83-105, 1936, de Gruyter, Berlin.

² Draper, J., *London, Edinburgh and Dublin Phil. Mag.*, 23, 401 (1843).

³ Mohr, F., and Wittstein, G., *Phot. Arch.*, 430, 1864.

⁴ Tyndall, *Jahresb. Chem.*, 108, 1868.

⁵ Fritzsche, J., *J. prakt. Chem.*, 101, 337 (1866); 106, 274 (1869).

⁶ Baumann, E., *Ann. Chem.*, 163, 317 (1872).

duced by the prolonged action of sunlight upon a wide variety of organic compounds were identified.

During the first two decades of the present century, the development of the subject of the kinetics of chemical reactions led Bodenstein, Nernst and others to attempt the interpretation of the data on the rates of photochemical reactions in terms of the law of mass action. The difference between the rates of a given reaction occurring in light and in darkness was at first attributed merely to an effect of the light in increasing the velocity constant in the simple mass law expression, no consideration being given to the possibility of a difference in mechanism in the two cases. Attempts were made, although unsuccessfully, by Wildermann⁷ to treat the function of the light energy in a fashion analogous to the manner in which Faraday treated electrical energy in the study of electrolysis.

In the case of a few reactions the attempt was made to introduce the intensity of the incident light I_0 in the expressions formulated for the reaction kinetics,⁸ as for example, $\text{rate} = k' I_0 [A]^m [B]^n$. Van't Hoff in 1904 introduced the assumption that the amount of substance transformed in a reaction is proportional to the amount of the light energy absorbed, rather than merely to the incident intensity, and thereby gave quantitative significance to the Grotthuss-Draper law. Attempts to determine whether or not all of the absorbed energy is effective photochemically were made, notably by Luther and Weigert⁹ for the anthracene-dianthracene equilibrium, by Goldberg¹⁰ for the photo-oxidation of quinine by chromic acid, and by Lasareff for the bleaching of dyes.¹¹

During this period there were also a number of theoretical studies of photochemical reactions, some dealing with mechanism and others with thermodynamic considerations.¹² Real progress had, however, to await the contributions of the physicist. In the first place, on the practical side, the development of the quartz mercury-vapor arc (Chapter 6) greatly stimulated the study of reactions following the absorption of ultraviolet rays, studies of the wave-length dependence of the yield soon appearing in great number. On the theoretical side, the development of the quantum theory (Chapters 1 and 2) for the first time permitted a beginning to be made in the approach to a satisfactory comprehension of the mechanism by which radiant energy may be absorbed by molecules. Before considering these mechanisms (Chapter 13) it is necessary to discuss the general physical laws of absorption.

The loss in radiant energy of a beam of light which occurs during its passage through a cell containing a liquid or a gas is ascribed to three processes; (a), reflection at the surfaces, (b) scattering by any dust particles in the gas or by colloidal particles in the liquid and (c) absorption by the molecules of the gas or liquid. The last of these is the only one of importance photochemically. In homogeneous pure liquids, scattering may usually be neglected.

Lambert showed that the absorption of approximately monochromatic light varies exponentially with the thickness of the absorbing layer, or $I_x = I_0 e^{-\beta x}$ in which I_0 and I_x denote the incident and transmitted light intensities, x is the

⁷ Wildermann, M., *Z. physik. Chem.*, **42**, 257 (1902); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910); *Chem. Abs.*, **4**, 1842 (1910).

⁸ Bunsen and Roscoe in the hydrogen chlorine reaction and Gros, O., *Z. physik. Chem.*, **37**, 157 (1901).

⁹ Luther, R., and Weigert, F., *Z. physik. Chem.*, **53**, 385 (1905).

¹⁰ Goldberg, E., *Z. wiss. Phot.*, **4**, 61 (1906).

¹¹ Lasareff, P., *Ann. Phys.*, **24**, 661 (1907); **37**, 812 (1912).

¹² Tian, A., *Compt. rend.*, **156**, 1601 (1913); Henri, V., *Soc. Franc. d. Phys.*, **12**, 2 (1911); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 1597 (1912); **156**, 889 (1913); **160**, 519 (1915).

thickness of the absorbing layer and β is a number characteristic of the absorbing substance and called its absorption coefficient. Its value varies with the wave-length in a manner characteristic of the substance.

In 1852, Beer found that in the case of solutions, β is proportional to the concentration, c , of the absorbing component. β may therefore be replaced by αc , α being the absorption coefficient of the absorbing component of the solution. (In cases in which the solute is modified by or reacts with the solvent, Beer's law does not hold.) About this time, Stokes made extensive studies of the phenomenon of fluorescence, which consists in the emission of light of certain wave-lengths by a substance during the time in which it is being irradiated by light of (usually) other wave-lengths. He found that the wave-lengths of the emitted rays are greater than those of the exciting rays. (Stokes's Law.)

THE EINSTEIN PHOTOCHEMICAL EQUIVALENCE LAW

Of the utmost importance to the subsequent development of photochemistry was the derivation by Einstein¹³ of the photoequivalent law which states that each absorbed quantum should cause one light-absorbing molecule to react. The derivation of this law, obtained from Planck's radiation law by thermodynamic reasoning, lies beyond the scope of this book. It implies that the number of molecules which have absorbed monochromatic radiant energy may be obtained by dividing the total absorbed energy in ergs (measured physically) by the energy $h\nu$ of a single quantum of light of the frequency employed. To facilitate the evaluation of the quanta of various frequencies commonly employed in photochemistry, Bodenstein and Wagner¹⁴ proposed to employ the term einstein for the energy of N (the Avogadro number, 6.06×10^{23}) light quanta, this being the energy absorbed when each molecule of a gram-molecular weight of a substance absorbs a quantum of radiant energy. They suggested that the intensity of absorbed light be expressed in einsteins absorbed per liter per second.

The idea that the rate of a photochemical reaction may be determined by the number of light quanta absorbed per second had been expressed by Stark as early as 1908¹⁵ preceding the derivation of the photochemical equivalent law by Einstein. Stark believed the primary effect of the light absorbed to be a loosening of the valence electrons, rendering the molecule chemically active. He also distinguished between the primary process of the absorption of light by a molecule and the subsequent secondary processes initiated by the light-changed molecule.

The value of the einstein is commonly expressed in kilocalories for photochemical work. It may be calculated by multiplying the frequency by Planck's constant h (6.54×10^{-27} erg-seconds) and by N (6.06×10^{23}) and dividing the result by 4.182×10^{10} to convert ergs into kilocalories. If the wave-length in Ångström units is first converted into the wave-number by the aid of the graph at the right of Figure 103 it may easily be converted into kilocalories by multiplication by the factor 0.00285. Even this calculation may be avoided by the use of the curve (A vs. kcal.) in the same figure.

An appreciation of the magnitude of the einstein at various wave-lengths is of value in enabling one to predict the possibility of effecting a reaction of known activation energy by the use of a given wave-length known to be absorbed by the reacting system.

¹³ Einstein, A., *Ann. Physik*, **37**, 832 (1912); **38**, 881 (1913).

¹⁴ Bodenstein, M., and Wagner, C., *Z. physik. Chem.*, **3B**, 456 (1929).

¹⁵ Stark, J., *Physik. Z.*, **9**, 898 (1908).

It is convenient to remember that 10,000A, where the wave-number is also 10,000, corresponds to 28.47 kcal. Then at 5000A the wave-number will be twice as great since it is the reciprocal of the wave-length which is half of 10,000A; the heat value will, therefore, be twice 28.47 or 56.94 kcal. The wave-length, 4000A corresponds to 71 kcal., 3000A to 94.6 kcal. and 2000A to 142.1 kcal. In the x-ray region the values become enormous, but in the far infrared they decrease to such small values as 0.285 kcal. at 100 μ .

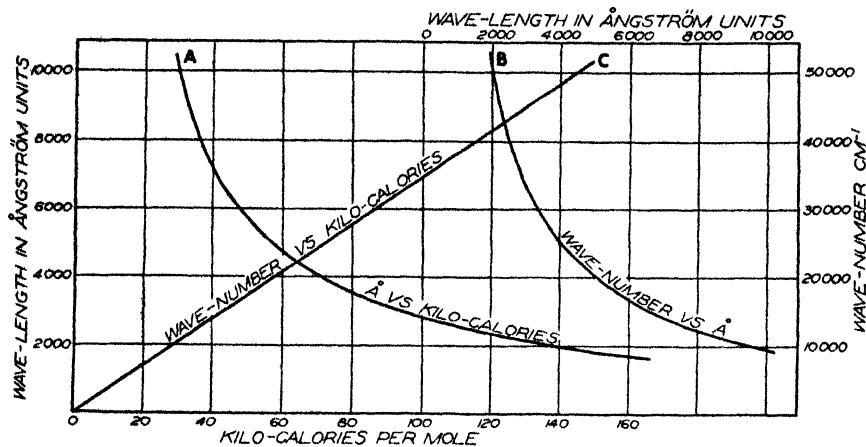


FIGURE 103. Graphs for Conversion of Wave-lengths and Wave-numbers into Kilo-calories per Mole and for Conversion of Angstrom Units into Wave-numbers.

Most photochemical reactions follow upon a process of absorption in which the configuration of the valence electrons has been in some manner altered, and it will be shown in Chapter 13 that visible or ultraviolet radiation is usually required to produce such an electron shift. In the infrared region, the absorbed energy is usually insufficient to produce such effects and instead serves only to alter the rotational motion of the molecule as a whole or the vibrational motion of its component atomic nuclei with respect to each other.¹⁶ There is no fundamental distinction between the reactions due to visible or ultraviolet light and it is not feasible to discuss their effects separately. In order adequately to discuss the effects produced by ultraviolet light it will frequently be necessary to disregard the limitation set by the title of this book and to discuss many reactions due to the absorption of visible light.

Little is known of reactions which may be induced in the regions between the Schumann and the usual x-ray regions. Palmer¹⁷ has noted that radiations from a hydrogen discharge tube passing through a fluorite window into air cause the formation on the outside of the window of a film with metallic luster (soluble in alcohol) which probably is calcium oxyfluoride, and upon the latter a white powder insoluble in water and soluble in dilute hydrochloric acid. Both deposits impede the passage of rays of wave-lengths between 1250 and 1500A.

Reactions Produced by X-Rays. These reactions have received far less study than those produced in the visible and ultraviolet regions. The direct photo-

¹⁶ Mecke, R., *Trans. Faraday Soc.*, **27**, 359 (1931).

¹⁷ Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).

chemical absorption of the radiation plays a role subordinate to the effects of photoelectrons. The enormous energies of the x-rays make it possible for one quantum on ionizing a molecule to endow the resulting photoelectron with great amounts of kinetic energy.¹⁸ Subsequent effects bear some resemblance to the reactions produced by the bombardment of a substrate with a stream of high-velocity electrons.¹⁹

According to Risse,²⁰ and Fricke and Brownscombe²¹ pure, oxygen-free water is not decomposed by x-rays. Comparatively few inorganic reactions have been studied. Noteworthy among these are the hydrogen-chlorine combination,²² the decomposition of hydrogen peroxide and of potassium persulfate,²³ and certain changes induced in ferrous sulfate,²⁴ chromic acid,²⁵ iodine²⁶ and on photographic plates.²⁷ Among organic compounds, chloroform and iodoform have been the most extensively studied; hydrogen halides are liberated along with other less investigated products.²⁸

General reviews of the chemical effects of x-rays, which in the main are much less extensive than those produced by ultraviolet rays, have been given by Glocker,²⁹ Günther,³⁰ Clark and Pickett,³¹ and by Fricke.³² Fricke states that a peculiarity of x-ray action is that it frequently involves the production of molecules with unusually high energy states, such as water molecules with at least 91 kcal. per gram molecule.

The Infrared Region. With the possible exception of certain explosions, which may be influenced by infrared radiations,³³ no established case of a chemical reaction brought about by these radiations could be cited by Daniels in 1928.³⁴ Many attempts were, however, made to find such reactions because of the stimulus of the radiation theory of the origin of the activation energy for chemical reactions, now nearly universally abandoned. This theory which was first suggested by Trautz,³⁵ and elaborated by Lewis,³⁶ Perrin,³⁷ and others,³⁸ held that the necessary activation energy calculated from the temperature coefficient by the Arrhenius equation, is obtained by absorption by the

¹⁸ Dauvillier, A., *Compt. rend.*, **171**, 627 (1920).

¹⁹ For a further discussion of this topic, see Simons, L., *Brit. J. Radiology (Roentgen Soc., Sect. 23)*, **124** (1927), or the article of Failla, G., in Duggar, "The Biological Effects of Radiations," New York, McGraw-Hill, 1936.

²⁰ Risse, O., *Z. physik. Chem.*, **140**, 133 (1929).

²¹ Fricke, H., and Brownscombe, E. R., *Strahlentherapie*, **26**, 319 (1929); **24**, 749, 757 (1927); Fricke, H., and Washburn, M., *Phys. Rev.*, **40**, 1033 (1932); Fricke, H., and Brownscombe, E. R., *Ibid.*, **44**, 240 (1933); Fricke, H., *J. Chem. Phys.*, **2**, 349 (1934).

²² Leblanc, M., and Volmer, M., *Z. Elektrochem.*, **20**, 494 (1914), Götzky, S., and Günther, P., *Z. physik. Chem.*, **26B**, 373 (1934).

²³ Glocker, R., and Risse, O., *Z. Physik*, **48**, 845 (1928).

²⁴ Shishacow, W., *Phil. Mag.*, **14**, 198 (1932); Fricke, H., *loc. cit.*

²⁵ Fricke, H., and Washburn, M., *loc. cit.*

²⁶ Bordier, H., *Compt. rend.*, **163**, 291 (1916).

²⁷ Eggert, J., and Noddack, W., *Ber. deutsche physik. Ges.*, **23** (1924); Günther, P., and Tittel, H., *Z. Elektrochem.*, **39**, 647 (1933); de Monceiz, A., *Compt. rend.*, **184**, 284 (1927); Villard, P., *Compt. rend.*, **184**, 131, 309, 352 (1927); **186**, 1669 (1928).

²⁸ Glocker, R., *Z. tech. Physik*, **7**, 571 (1926); *Z. Physik*, **43**, 827 (1927); **46**, 764 (1928), Günther, P., *Angew. Chem.*, **46**, 627 (1933); Hill, D., *J. Am. Chem. Soc.*, **54**, 32 (1932).

²⁹ Glocker, R., *Z. tech. Physik*, **9**, 201 (1928).

³⁰ Günther, P., *Angew. Chem.*, **41**, 1357 (1928); *Ergebnisse tech. Röntgenkunde*, **4**, 100 (1934).

³¹ Clark, G. L., and Pickett, L. W., *J. Am. Chem. Soc.*, **52**, 465 (1930); Clark, G. L., and Coe, W. S., *J. Chem. Phys.*, **5**, 97 (1937).

³² Fricke, H., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 55 (1935).

³³ David, W. T., *Proc. Roy. Soc.*, **108A**, 617 (1925).

³⁴ Daniels, F., *Chem. Rev.*, **5**, 56 (1928).

³⁵ Trautz, M., *Z. wiss. Phot.*, **4**, 160 (1906); *Z. anorg. Chem.*, **102**, 81 (1917).

³⁶ Lewis, W. C. M., *J. Chem. Soc.*, **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920).

³⁷ Perrin, J., *Ann. Phys.*, **11**, 5 (1919), *Trans. Faraday Soc.*, **17**, 546 (1922); *Compt. rend.*, **187**, 913 (1928).

³⁸ Baly, E. C. C., *Phil. Mag.*, **40**, 1, 15 (1920); *Rec. trav. chim.*, **41**, 516 (1922).

0.032 to 0.104 for the third, extremely high for the fourth, from 0.28 to 1.7 (dependent upon the presence of other gases) for the fifth, 0.024 to 0.25 for the sixth, and 0.25 for the last.

It is important to note the manner in which experiments made with three separate wave-lengths of approximately monochromatic light in the hydrogen iodide decomposition and with two wave-lengths in the case of that of hydrogen bromide afforded a strong confirmation of the theory. Since the magnitude of the quantum increases as the wave-length decreases, it is evident that for the same total amount of energy absorbed at different wave-lengths, the number of quanta absorbed decreases as the wave-length decreases. Therefore, the yield of a given process should be less when the same total energy is employed at a shorter than at a longer wave-length. In the hydrogen iodide decomposition, Warburg found that the ratio of moles decomposed to the calories absorbed (multiplied by 10^5) decreased from 2.08 at 2820Å to 1.85 at 2530Å and 1.447 at 2070Å. The expected values calculated upon the basis of the Einstein law were 1.003, 0.89 and 0.73, respectively. These were in each case very close to half of the observed values. Therefore, in each case, the quantum yield was two. The results in the hydrogen bromide decomposition were very similar.

Warburg was also able to suggest a reasonable explanation of the quantum yield of two by assuming the primary process of absorption by the hydrogen iodide or bromide to consist in a dissociation of these molecules into atoms. A relatively simple sequence of secondary reactions, supported on thermodynamic grounds by Nernst, accounted for the observed quantum yield of two. In this way, granting the correctness of the assumed mechanism of the primary process, the observed quantum yield, despite the fact that it was not unity, could be regarded as a confirmation of the theory. The opinion gradually gained ground that when all factors were taken into account, it would be possible to devise mechanisms for the primary processes and secondary reactions for those photochemical reactions in which extreme values of the quantum yields at first sight appeared less favorable to the theory.

In summarizing his work, Warburg stated⁵⁸ that the law has been proved to apply when the quantum absorbed is greater than the energy of dissociation, although in certain cases collisions of the products of dissociation with molecules of foreign gases may lead to a dissipation of their energy so that the law is apparently not followed. He also recognized at this time that in the case of reactions effected by the absorption of quanta smaller than the heat of dissociation, the mechanism of the primary process may involve the formation of excited rather than dissociated molecules. (This type of mechanism will be considered in more detail subsequently.) In this case, under certain conditions, complicating processes may lead to a dissipation of a portion of the energy of some excited molecules so that the quantum yield may be reduced.

Perhaps the present position with regard to the Einstein law has been most clearly stated by Taylor⁵⁹ who avoids the idea of equivalence implied by earlier statements of the law by giving it in the form of this Second Law of Photochemistry:

"The absorption of light is a quantum process involving one quantum per absorbing molecule or atom. The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." Henri and

⁵⁸ Warburg, E., *Naturwiss.*, 47, 1058 (1924).

⁵⁹ Taylor, H. S., *J. Phys. Chem.*, 32, 516 (1928).

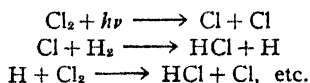
Wurmser⁶⁰ recognized the importance of the nature of the primary process in determining the mechanism of a photochemical reaction and discussed the manner (see Chapter 14) in which fluorescence and absorption spectrum studies may be employed in determining the nature of the primary process.

Despite general acceptance of the Einstein law, the possibility has been suggested that in certain cases one quantum of incident energy may activate more than one molecule of the absorbing substance. Basu⁶¹ suggested, possibly as an outcome of Raman spectrum interpretations (Chapter 13), that the incident quantum uses part of its energy in activating the molecule it strikes, and that the remainder is scattered and may activate another molecule.

Investigations of quantum yields have been and are still being carried out extensively because they provide data for testing proposed mechanisms for the reactions studied. Quantum yields are determined for various incident wavelengths of radiation for each new photochemical reaction investigated. The influence upon the yields of many factors, including temperature, variations in the intensity of light, the effects of changes in pressure in gaseous reactions and of concentration in solutions, the effects of different solvents, catalysts and inhibitors, are being actively studied. The more detailed discussion of these topics is given in connection with the individual reactions considered in subsequent chapters.

CHAIN REACTIONS

Allusion has been made to the fact that in certain reactions high quantum yields have been observed. Thus in the hydrogen-chlorine combination, it was stated that the quantum yield was of the order of a million. To explain this, Nernst⁶² proposed on thermodynamic grounds the possibility of the following cycle of reactions:



The last two of these reactions evolve heat and can occur spontaneously and be repeated until the hydrogen and chlorine are consumed. Other reactions are conceivable, but are limited in extent. If two chlorine atoms could combine to form a chlorine molecule, they might be expected to dissociate again on absorption of another quantum of radiation. There is, however, an even more cogent reason why neither this process nor the combination of two hydrogen atoms to form molecules can occur to any considerable extent. The combination of two chlorine atoms is exothermic to the extent of 58.5 kcal. For the production of a stable molecule by a collision of two atoms it would be necessary for the energy of recombination to be removed in some manner or the atoms would move apart again. If, however, two atoms of chlorine (or of hydrogen) should chance to collide at the same time with a molecule of an inert gas or with the wall of the reaction vessel, the excess of energy might be imparted to the inert gas molecule or to the wall so that a stable molecule of chlorine (or of hydrogen) might be produced. The inability of atoms to combine to form molecules by two-body collisions thus provides one of the reasons which make it possible for the reactions written above to be so often repeated and thereby make the quantum yield so enormous. In the language of physical chemistry, the chains are said to be long.

⁶⁰ Henri, V., and Wurmser, R., *J. phys. Radium*, 8, 289 (1927).

⁶¹ Basu, K. P., *J. Phys. Chem.*, 33, 1200 (1929).

⁶² Nernst, W., *Sitzb. Berlin Akad. Wiss.*, 65 (1911).

Although Nernst set up the reaction chain just discussed, he did not at that time suggest all of the details; many others have contributed to the building up of our present concept of chain reactions. Nernst calculated that a similar cycle would be impossible in the case of the combination of hydrogen and bromine, because the reaction $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$ is endothermic. Actually, a mixture of hydrogen and bromine is not light sensitive at ordinary temperatures, although a chain reaction occurs at higher temperatures. A further discussion of the more detailed reasoning in regard to these reactions and also the hydrogen iodide decomposition will be given in the chapter on reactions in the gas phase. (Chapter 17.)

Many chain reactions are subject to inhibition by certain substances, which when present in traces, break the chains and lower the yields. A general discussion of the methods of determining the mechanisms of chain reactions has been given by Noyes.⁶³

In interpreting the kinetics of chain reactions, three processes require consideration, (a) the chain starting process, (b) the chain terminating process and (c) the chain continuing process.⁶⁴

The Nature of the Primary Process. During recent years an increasing amount of attention has been devoted to an exact determination of the nature of the primary processes of light absorption and the molecular changes affected thereby. Although the book by Kistiakowsky on Photochemical Processes (1928) was predominantly concerned with the kinetics of a number of complete reactions, an indication of the recent shift in emphasis is to be found in the fact that the "Foundations of Photochemistry" by Bonhoeffer and Harteck (1933) devotes 182 pages to the primary process, 39 to secondary reactions and only 59 to the kinetics of overall reactions. At present, efforts are being made to increase our knowledge of the secondary reactions.

Besides the Warburg theory of dissociation as the primary process, others have been proposed. Recent studies indicate, however, that the production of atoms or free radicals either by direct dissociation following the absorption of a quantum or by predissociation (a process described in Chapter 14) is the most commonly encountered primary process.

The early views were rather indefinite. Stark⁶⁵ thought the primary effect to be a loosening of valence electrons, rendering the molecules chemically active ("intramolecular photoelectric effect"). Baly and Rice⁶⁶ considered ordinary molecules as condensed systems which are non-reactive until opened up, and discussed the relation of absorption bands and fluorescence phenomena to this loosening process. An important paper historically was one in which Stern and Volmer,⁶⁷ on the basis of the then current interpretation of band spectra, took issue with the dissociation mechanism proposed by Warburg for the reactions of the hydrogen halides. These authors, influenced by the Bohr theory of the excitation of atoms, explained the primary process of light absorption by molecules in terms of an analogous elevation of the energy level of the molecule by the energy of the absorbed quantum. In this way they made somewhat more precise what is implied in the activation of molecules, a term which had been used earlier by Luther. They discussed particularly the possible ways in which excited molecules might

⁶³ Noyes, W. A., Jr., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 32 (1935), see also Semenov, N., *Acta Physicochim. U.R.S.S.*, **3**, 245 (1935).

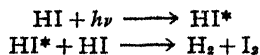
⁶⁴ Rollefson, G. K., *J. Phys. Chem.*, **42**, 773 (1938).

⁶⁵ Stark, J., "Prinzipien der Atomdynamik," Leipzig, S. Hirzel, II, 207 (1911).

⁶⁶ Baly, E. C. C., and Rice, F. O., *J. Chem. Soc.*, **101**, 1475 (1912).

⁶⁷ Stern, O., and Volmer, M., *Z. wiss. Phot.*, **19**, 275 (1920).

dispose of their energy of excitation. In the first place the energy might be lost by re-emission (fluorescence). A second possibility is the loss of the energy of excitation by inelastic collisions with other molecules, involving conversion of energy of excitation into heat energy. The third and most important possibility is that the excited molecules on colliding with other molecules might utilize this excess energy as energy of activation in bringing about chemical reactions. Thus an activated hydrogen iodide molecule (denoted by *) on colliding with a normal molecule might cause a reaction in which a molecule of hydrogen and one of iodine are produced.



In this way it would be possible to explain the quantum yield of two which had been determined experimentally by Warburg.

At the time it was put forward, this view had much to recommend it. Data were being contributed by physicists on the fate of excited atoms and the manner in which the loss of their energy by fluorescence could be quenched or lessened by the presence of inert gas molecules which by collisions could remove the energy. An extension of these considerations to photochemical reactions offered an attractive opportunity for explaining the decreases in quantum yields of gas reactions often observed to occur in the presence of increasing concentrations of foreign non-absorbing gases. Furthermore, at this time relatively little was known of the behavior of atoms or free radicals and their postulation as intermediates by Warburg appeared unnecessarily artificial. Warburg indeed gave as the criterion for the occurrence of dissociation in the primary process the stipulation that the quantum energy of the absorbed radiation must be larger than the heat of dissociation of the molecules, and recognized that the absorption of lesser quanta could lead only to the production of excited molecules. For these reasons, attention during the early 1920's was predominantly devoted to the activated molecule theory of the primary process. Noddack⁶⁸ explained the lowering of the yield in the reaction between chlorine and trichlorobromomethane in carbon tetrachloride which accompanies increasing dilution by the solvent on the basis of this theory. The more frequent collisions of the activated molecules with indifferent carbon tetrachloride molecules deactivated them so that the photochemical reaction had less chance of occurring. It was also pointed out by many that if an activated molecule did not collide with a molecule with which it might react within its life period (10^{-8} - 10^{-9} second)⁶⁹ it would lose some of its energy by fluorescence; if, on the other hand, it collided with an indifferent molecule it could lose its energy in the collision. In a gas at normal pressures the loss of energy by fluorescence would not be expected to be important, this effect becoming pronounced only when the time interval between collisions of the excited molecules with the reactant molecules becomes comparable with the mean life of the excited state.

Attempts were made to extend the theory of activated molecules to account for chain reactions, the assumption being made that such an excited molecule enters into reaction with a normal molecule and produces another excited molecule as one of the products in a manner analogous to that in which atoms functioned in the chain theory of Nernst. It need only be said here that such energy chains have been shown to involve certain difficulties and that, in the main, there is rarely any necessity for assuming their occurrence in explaining photochemical

⁶⁸ Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921).

⁶⁹ Cf. Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 283 (1925).

processes. Elaborate attempts were also made to picture the change involved in activating molecules in terms of the orbits in which the valence electrons move.⁷⁰ Such attempts have been rendered unnecessary by developments of the theory of valence and of molecular energy states.

Brief mention may be made at this point of an early theory of Weigert⁷¹ which assumed that at least two molecules of gaseous halogens participate in the absorption process, an electron being believed to be displaced from one to the other. The resulting molecular complex acted as a nucleus at which subsequent reactions proceeded. This theory has not survived, although a vestige remains in the modern treatment of the photochemical processes occurring in alkali-halide crystals.

By 1924, Bowen,⁷² in comparing the mechanisms (dissociation versus excited molecule) of the primary process involved in the photochemical reactions by which the hydrogen halides are formed showed that the dissociation theory gives a quantitative explanation of all the experimental facts if due consideration is given to the heats of reaction and if it is assumed that a large evolution of heat favors a spontaneous reaction and that an endothermic secondary reaction does not proceed. He pointed out that a clarification of the then conflicting points of view in regard to the nature of the primary process awaited a physical interpretation of the data of the band absorption spectra of gases. The most marked feature of the development during recent years has been the application of the theory of band spectra to the interpretation of the primary processes of photochemical reactions. For this reason the next chapter digresses to give a brief introduction to the theory of the origin of band spectra, after which it becomes possible in Chapter 14 to discuss the contributions which spectroscopy is able to make to an understanding of the nature of the primary process in photochemical reactions occurring in the gas phase.

⁷⁰ Waldbauer, L., and Patton, I. J., *J. Phys. Chem.*, **31**, 1433 (1927).

⁷¹ Weigert, F., *Ann. Physik*, **24**, 243 (1907); *Z. Elektrochem.*, **28**, 456 (1922); Weigert, F., and Kellermann, K., *Z. physik. Chem.*, **107**, 1 (1923); Weigert, F., *Ibid.*, **102**, 416 (1922); **106**, 407 (1923). See, for objections, Kornfeld, G., *Z. physik.*, **108**, 118 (1924).

⁷² Bowen, E. J., *J. Chem. Soc.*, **125**, 1233 (1924); *Trans. Faraday Soc.*, **21**, 543 (1925).

Chapter 13

Molecular Spectra and Their Relation to Photochemistry

Early workers on the absorption or emission spectroscopy of molecules used spectroscopes of low resolving power and observed spectra characterized by more or less regularly recurring flutings or bands. These apparently continuous bands gave rise to the term "band spectra," really a misnomer since instruments of higher resolving power have long since revealed the fact that in many cases, the "bands" in the spectra of gaseous molecules are really composed of great numbers of finely spaced lines.

Molecular spectra have been very actively investigated within the last two decades. The literature dealing with them is of vast proportions and is couched in a somewhat unfamiliar notation, unfortunately necessary because of the complexity of the interrelations between the forms of motion characterizing molecular energy states, the transitions between which give rise to the many lines. In the study of the emission spectra of molecules much effort has been required merely to identify the molecule or molecular fragment giving rise to a given spectrum or arrangement of lines and bands under the experimental conditions of excitation. In many instances it has been demonstrated that the spectrum must be attributed to the presence of molecules of a type unfamiliar to a chemist (BO, He₂, BaH, etc.).

Early investigations were limited to the accurate measurements of the wavelengths of the many lines observed in the emission or absorption spectra of various substances produced under definite experimental conditions. Later phases of the work were concerned with the identification of the molecules responsible for these spectra, and, following this, with the classification of the lines into bands, of the bands into groups of bands, and of these groups into larger series. Next came the representation of these observed facts by mathematical expressions. Only in the past thirty years has it been possible to make physical interpretations of the relationships thus demonstrated.

The study of molecular spectra has provided the chemist with a tool which has yielded data valuable in fields remote from that of photochemistry. The spectra provide information as to the structures, sizes and shapes of molecules, have led to the discovery of the isotopes of several elements and have furnished values for heats of dissociation, bond strengths, heat contents, entropies, specific heats, free energies, equilibrium constants and heats of activation in many cases more readily and more accurately than are secured by the older methods of thermochemistry.¹ Progress in the application of the methods of wave mechanics to the interpretation of band spectra has been so rapid as to have led Kemble² to

¹ Giaque, W. F., and Wiebe, R., *J. Am. Chem. Soc.*, **50**, 101, 2193 (1928); **52**, 4808, 4816 (1930); **53**, 507 (1931); Godnev, I. N., *Ibid.*, **58**, 180 (1936); Kassel, L. S., *Phys. Rev.*, **43**, 364 (1933); *J. Am. Chem. Soc.*, **55**, 1351 (1933); *J. Chem. Physics*, **1**, 576 (1933); Zeise, H., *Z. Elektrochem.*, **39**, 758 (1933); Franck, J., *Ibid.*, **36**, 581 (1930); Bryant, W., *Ind. Eng. Chem.*, **25**, 820 (1933); Rodebush, W., *Chem. Rev.*, **9**, 319 (1931); Kassel, L. S., *Chem. Rev.*, **18**, 277 (1936); Witmer, E., *J. Am. Chem. Soc.*, **56**, 2229 (1934).

² Kemble, E. C., *J. Frank. Inst.*, **206**, 27 (1928).

express the hope that "in a few years we may understand the fundamental principles of molecule formation as definitely as we now understand the principles of dynamo design."

The complexities of spectra and the extensive mathematical equipment required for their interpretation make this a field for specialists. Fortunately, a detailed knowledge of this field is not essential to an understanding of much of the work in photochemistry. The discussion in this chapter is intended only to furnish the chemist not versed in spectroscopy with enough of the present viewpoint regarding molecular spectra to permit him to comprehend the manner in which the character of the spectrum within a given wave-length region shows whether the absorption has produced excited molecules or has led to a dissociation of the molecule into atoms or free radicals. The character of the molecular spectrum thus gives a clue to the nature of the primary process of absorption. For the most part, only the spectra of diatomic molecules will be considered, since these have been more completely interpreted than have the vastly more complicated spectra of polyatomic molecules.

Representative of the band spectra of diatomic molecules is that of phosphorus nitride, a portion of which is reproduced in Figure 104. Each of the dark regions which fades out gradually from a sharp edge is known as a band. Some molecules produce spectra in which the fading from the edge of the bands to more and more widely separated and weaker lines extends toward the shorter wave-lengths. In the spectra of others the opposite is true. The bands are accordingly said to be degraded toward the violet or toward the red.

The edges of the bands recur in a somewhat regular sequence and so form a band group. Furthermore, over wider spectral ranges, the various groups of bands may also follow in sequence to form a system of bands. The complete emission spectrum of a substance may under certain circumstances consist of several band systems. Cyanogen, for example, has one system between 4000 and 5000A and another in the red. Different portions of the complete spectrum may be revealed by the use of different methods of excitation. The complete spectrum of a diatomic molecule composed of unlike atoms may extend from the far infrared to far in the ultraviolet.

Deslandres,³ a pioneer in the empirical study of molecular spectra, demonstrated relations between the wave-numbers of the lines of a band and also between those of the heads of the bands of a group. As in the case of atomic spectra, progress in the interpretation of such relationships came only with the application of the quantum theory. The wave-numbers of the individual lines depend upon the differences between energy states of the molecule. In discussing the possible energy levels of a molecule there must be considered certain molecular and intramolecular motions which were not encountered in the discussion of the energy levels of atoms. The molecule may rotate as a whole about its center of gravity and the two atomic nuclei may vibrate with respect to each other along the line joining their centers. Each of these types of motion is quantized, only discrete rotational and vibrational energy levels being possible. In addition, as in atomic spectra, transitions between electronic energy levels must be considered.

Even before the advent of the Bohr theory of the quantization of the electronic states of atoms, Bjerrum⁴ suggested that transitions between various rotational

³ Deslandres, H., *Compt. rend.*, 103, 375 (1886); 104, 972 (1888); 134, 747 (1902); 138, 317 (1904); *Ann. Chim. Phys.*, 15, 5 (1888); *J. de phys.*, 10, 276 (1891).

⁴ Bjerrum, N., *Nernst Festschrift*, 90 (1912); cited in Baly, E. C. C., "Spectroscopy," Vol. 3, London, Longmans Green, 1927.

FIGURE 104. Band Spectrum of a PN Molecule (From Herzberg, "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937).

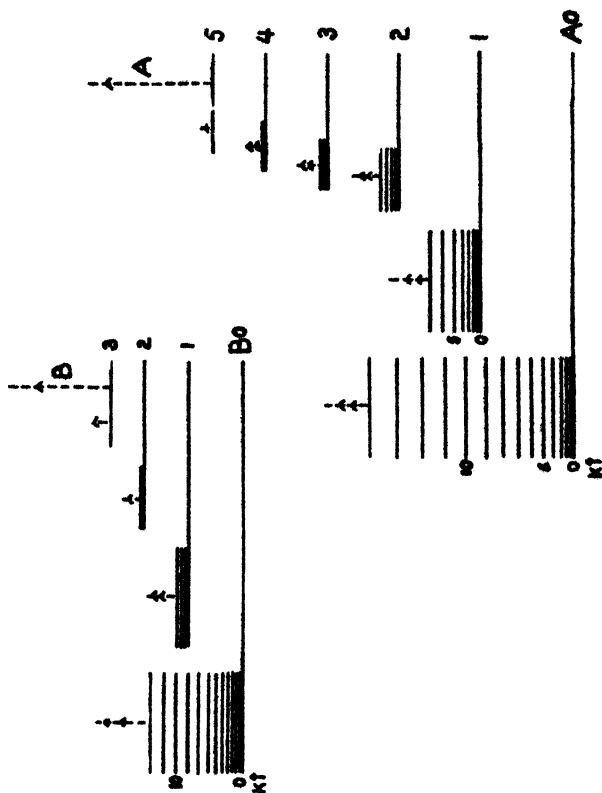


FIGURE 105. Schematic Energy Level Diagram for Diatomic Molecule (Mulliken, *Chemical Reviews*).

states of the molecule might account for the energy differences corresponding to the lines in the far infrared spectra of diatomic molecules. Schwarzschild⁵ employed a series of integral quantum numbers in an expression by which the quantized moment of momentum of the rotating molecule could be used in calculating the wave-numbers of the various lines corresponding to shifts between rotational states. Heurlinger⁶ introduced vibrational quantum numbers for dealing in a similar manner with the to-and-fro oscillations of the nuclei with respect to each other. Kratzer⁷ developed the theory of the vibrations of an anharmonic oscillator in terms of the approximation that the motions of rotation and vibration do not mutually influence each other. He also employed selection principles analogous to those employed in atomic spectra for the restriction of the transitions which are permitted between various rotational and vibrational states.

In general, then, three forms of energy contribute chiefly to the total energy of each state between which the line-producing transitions occur. The total energy may be represented by $E_{el} + E_{vib} + E_{rot}$. The order in which these have been listed is that of decreasing magnitudes of the energy contributions. In more accurate expressions, the effects of interactions between the various forms of motion must be taken into account. In the energy level diagram of a molecule there is for each electronic state a series of more closely spaced vibrational states designated by successive quantum numbers, and for each vibrational level a series of still more closely spaced rotational levels, also designated by integral quantum numbers. (Figure 105.)

The electronic state of lowest energy is termed the ground state; the other electronic states are excited states, the excitation energies being of the same order of magnitude as those of excited atoms. The successive energy increments between the electronic states vary in different molecules from about 1 to 10 electron-volts, corresponding to 1 to 10 times 23 kcal. The lines produced by transitions between such levels will lie in the visible or ultraviolet regions of the spectrum. Usually the number of electronic levels of a molecule available for transitions to produce lines in the accessible portions of the ultraviolet is much smaller than in the case of atomic spectra. Electronic term series are observed only in exceptional cases. The series limits corresponding to the ionization potentials of molecules are rarely encountered in the spectra most frequently referred to in the following chapters.

The separation of the vibrational levels is usually only 0.1 to 0.01 as great as that between the electronic levels (or about 1000 wave-numbers). The difference between rotational levels is very small, about 0.01 that between the vibrational levels, or from ten to 100 wave-numbers.^{7a} Transitions between terms in accordance with certain selection principles give rise to the spectral lines, the wave-numbers of which are readily obtained by subtraction of the values of the energy levels (terms) expressed as wave-numbers. In the most general case in the visible and ultraviolet regions, the lines are due to transitions in which the electronic, vibrational and rotational energies each suffer change. For a given electronic shift, there may be a diversity of simultaneous changes in the vibrational and rotational levels. This accounts for the great number of lines of molecular spectra. Transitions between two electronic levels give rise to a band system and those between other electronic levels to other band systems. Each band in the

⁵ Schwarzschild, K., *Preuss. Akad. Wiss., Sitzber.*, 548 (1916).

⁶ Heurlinger, T., *Physikal. Z.*, 20, 188 (1919); *Z. Physik*, 1, 84 (1920).

⁷ Kratzer, A., *Z. Physik*, 3, 289 (1920).

^{7a} In the light molecules, H_2 , He_2 , LiH , the rotational levels are more widely separated.

series comprising a single band system arises from a shift in the vibrational quantum number superposed upon one and the same shift between electron levels. The many fine lines which make up the structure of each band are determined in analogous fashion by the possible rotational shifts which may accompany the electronic and vibrational shifts which locate the position of the band edge.

Spectra may be encountered in the production of which neither electronic nor vibrational transitions have occurred. Since in these the transitions are exclusively between rotational states, such spectra are called pure rotation spectra. Since the rotational states lie very close together, transitions between them involve the emission or absorption of but very small amounts of energy so that the corresponding rotational lines have very low frequencies and lie far in the infrared. In practice, these lines are observed only in absorption spectra and have been comparatively little studied because of experimental difficulties. During the production of such spectra the molecules are always in the ground electronic state.

The frequencies in the near infrared region correspond to greater energy differences between terms, so that in their production certain transitions between the more widely separated vibrational levels are involved. Each such transition corresponds to a band, and as previously stated, each line within the structure of a given band corresponds to a change in the rotational state as well as that vibrational change which is concerned in the production of every line within that band. These near infrared spectra originating in simultaneous vibrational and rotational transitions are known as rotation-vibration spectra.

In the visible and ultraviolet regions electronic transitions are concerned and are accompanied by simultaneous vibrational transitions each producing a band and by rotational transitions responsible for the lines composing each band. Thus, each line in such a band corresponds to the same electronic shift and to the same vibrational shift, but the vibrational shift is different in the case of each line of each of the other bands. The origin of each band may be located by the frequencies corresponding to vibrational transitions between the zero rotational levels of successive vibrational levels, that is, the frequency is $\nu = \nu_{v+1} + \nu_{v,0}$, corresponding to $\nu_{\text{rot}} = 0$.

In the production of near infrared absorption spectra, the limited energy in each absorbed quantum usually suffices to excite but a very few vibration levels so that but a few bands (one to three or four) can appear. But the number of bands in the visible or ultraviolet regions accompanying each electron shift may be much greater, the vibrational quantum numbers may reach ten or more, and the spectra are accordingly much more complex. Molecules composed of two like atoms (H_2 , N_2 , etc.) exhibit no absorption in the infrared from 100μ to 1μ and lack pure rotation and rotation-vibration spectra. This does not mean that such molecules lack rotational or vibrational energy but indicates only that these symmetrical molecules lack the electrical moments whose existence is a prerequisite for interaction with electromagnetic radiations. When an electronic excitation has been brought about in such a symmetrical molecule, the resultant electronic structure is such as to make the molecule an electrical dipole capable of interacting with electromagnetic waves. For this reason the type of information yielded for heteropolar molecules by infrared rotation-vibration spectra can be obtained in the case of homopolar molecules only in the visible or ultraviolet regions. Even then, the spectra of these bands will be due to the transitions between rotational and vibrational states of the electronically excited molecules rather than that of the molecules in the ground electronic state. Information

regarding the vibrational and rotational levels of homopolar molecules may, however, be derived from studies of the Raman spectra to which brief reference is made in another section.

In general, the far infrared spectrum yields information about the rotational levels in the ground or electronically unexcited state of heteropolar molecules, and the near infrared region does the same for both the rotational and the vibrational levels. Similar information regarding the vibrational levels of electronically excited molecules is obtained from the series arrangement of the visible and ultraviolet bands; fine structure studies of the individual bands in these regions give information about the rotational term separations. To obtain similar data for the ground state it would be necessary to utilize the experimentally more difficultly accessible infrared spectra, or else to use the newer Raman spectra.

PURE ROTATION BANDS AND THE INFORMATION THEY YIELD

Spectra resulting from transitions between purely rotational states lie in the far infrared from 50μ to 200μ . Those of diatomic molecules consist of a series of equidistant lines, the separation of which yields valuable information regarding the molecular dimensions.

In a diatomic molecule rotating as a whole about an axis through its center of gravity, one of the three possibilities for rotation has a zero moment of inertia and the other two are equal. There is accordingly only one series of rotational quantized energy states which needs to be considered. The energies of the states are determined by the integral quantum numbers and by the moment of inertia of the molecule. This latter in turn is dependent upon the masses of the atoms composing the molecule and their separation. It is thus evident that, since the masses of the atoms are known, measurement of the energies of the various rotational states should furnish important information in regard to the sizes of the molecules. The manner in which this may be done lies beyond the scope of this book. This topic is mentioned merely to indicate the nature of the information it is possible to derive from band spectra.

The wave-number of a rotational state is given by $\frac{h}{8\pi^2 I} m(m+1)$ in which m may be zero or an integer and I is the moment of inertia. A selection rule states that the quantum number m may change by only one in a transition producing a line. Therefore, the wave-number of a line in this spectrum is given by the difference between two such terms, one having an m value one greater than the other. The expression for a given line reduces to $\nu = \frac{h}{4\pi^2 I} m$. The wave-number separation of a series of such lines corresponding to successive integral values of m thus permits of a calculation of I , the moment of inertia of the molecule. From the moment of inertia and the masses of the atoms, it is then possible to calculate the radius of the separation of the atomic nuclei. In exact work, a slight correction is required for a change in I due to centrifugal force in the higher rotational states.

THE VIBRATION-ROTATION BANDS

Absorption of a larger near infrared quantum produces a transition between vibrational states and is responsible for the production of a band. The corresponding wave-length, if there were no accompanying rotation, would locate the position of the band and would be called the zero line. Actually the absorption spectra of diatomic molecules fail to show this line since a selection principle requires that there be a rotational shift accompanying each vibrational transition. As previously stated, the series of lines composing the band is caused by a series of

simultaneous rotational transitions. The expression for the frequency of each of the lines of a band is given by

$$\nu = \nu_0 + \frac{h}{4\pi^2 I} m$$

in which ν_0 locates the origin of the band and the second term accounts for the effect of the rotational transition. As the rotational quantum number may either increase or decrease by one, the lines corresponding to transitions from each initial rotational state will be located on each side of ν_0 . The impression given by the band as a whole is that of two bands each composed of a number of sharp lines, the separation of which is similar to that of the lines of a pure rotation spectrum. The separation of the lines composing a band gives evidence regarding the rotational quanta and, as has been shown in the case of pure rotation spectra, from these much can be learned of the size and shape of the absorbing molecules.

The lines composing a band may be classified into two groups or branches. One series occurring on the long-wave side of the origin has the second term negative in the expression just discussed and is called the negative or P branch. A series in which m is positive occurs on the short-wave side of the origin and is called the positive or R branch. Transitions in which m does not change would give rise to a third branch called the zero or Q branch. Since they would violate the selection principle, the Q branch is usually lacking in the rotation-vibration spectra of the diatomic molecules, but is encountered in the spectra of polyatomic molecules as well as generally in electronic band spectra.

In the earlier attempts to interpret the successive bands in a vibration-rotation spectrum, the diatomic molecule was treated as an harmonic oscillator the vibrational states of which were quantized. The energy in a given state was denoted by $E_v = h\omega(v + \frac{1}{2})$, neglecting the contribution due to rotation. The necessity for the use of $\frac{1}{2}$ was found empirically, but has since been justified on theoretical grounds which cannot be here discussed. ω is the fundamental frequency of vibration of the nuclei and v is a quantum number which may be zero or an integer. When v is zero (the so-called vibrationless state) the molecule still possesses the vibrational energy $+\frac{1}{2}h\omega$. Successive integral values of v then give the successive vibrational states and transitions between these the zero lines of successive bands. To obtain the structure of the band use must be made of the more complete expression containing the rotational contribution to the energy state. From this theory but one infrared band would be expected. Its zero line is given by the fundamental frequency and its structure by the rotational effects. No matter whether the vibrational transition is from $v=0$ to $v=1$ or from $v=3$ to $v=4$, the zero line might be expected to be in the same position. (If the electronic structure of the molecule be altered as in the case of band spectra in the visible and ultraviolet regions, the fundamental frequency is, however, altered.) Actually, however, the diatomic molecule is not a true harmonic oscillator; the binding between the atoms is not elastic since the attractive force between them does not increase to infinity as they are more and more widely separated.

In the harmonic oscillator the restoring force K per cm. displacement x of the atoms from their equilibrium separation is proportional to this displacement.

$$K = -a x$$

The true frequency is related to a by the expression

$$\text{Frequency} = \nu c = \frac{1}{2\pi} \sqrt{\frac{a}{\mu}}$$

in which c is the velocity of light, ν the wave-number of the fundamental frequency and μ the "reduced mass" of the molecule, by which is meant the product of the masses of the two atoms divided by their sum. In the case of the non-harmonic oscillator, it is necessary to employ a power series in writing the binding force between the atoms,

$$K = -ax + bx^2 + cx^3 \dots$$

This means that higher powers, at least the second, of the vibrational quantum number must be employed in expressing the vibrational term wave-numbers.

$$\nu = (v + \frac{1}{2})\omega_0 - (v + \frac{1}{2})^2 x \omega_0.$$

Here x is a factor for the anharmonicity of the binding and determined by the coefficients in the power series written above. The differences between successive terms responsible for the origin of the bands are thus equal to $\omega - 2x\omega(v + 1)$. This makes it evident that several bands corresponding to different values of n may appear in a system. From this relation it appears that the separation of the successive bands of a system tends to decrease as the quantum number attains high values. Actually only a few bands are usually encountered in the near infrared spectra.

In polyatomic molecules,⁸ there may be several modes of vibration, including deformation vibrations in non-linear molecules. The resultant band spectra produced as a result of the interplay of these various forms of motion may be quite complex. The near infrared spectrum of ammonia, for example, contains 13 bands. In each series of bands those involving transitions between states of higher quantum numbers decrease rapidly in intensity, so that those capable of yielding accurate measurements are relatively few.

Raman Spectra. Much of the information regarding the vibration frequencies of various linkages can be more readily obtained by observations of their effects upon the scattering of visible and ultraviolet monochromatic radiations: in 1928, Raman⁹ observed that the ordinary radiation scattered by molecules in dust-free liquids or gases contains, besides the radiation of the same wave-length as the incident light, still other wave-lengths, usually of lower frequencies, together with some lines of lower intensity but of higher frequencies. The wave-numbers corresponding to the shifts of the frequency of the new lines in the scattered radiation from the frequency of the incident radiation are in general related to the frequencies of infrared bands. The importance of this new tool led to a large number of investigations of a wide variety of substances, solids, liquids, gases and solutions. The information secured with Raman spectra on the structure of organic molecules has been reviewed by Dadiou and Kohlrausch.¹⁰

The discussion of the physical aspects of the Raman effect lies beyond the scope of this work. Its value consists in part in the fact that it permits a determination of frequencies of vibration of molecules in their ground states and in part in that it is also applicable to homopolar molecules.

ELECTRONIC BAND SPECTRA

Electronic excitation is the chief alteration produced in a molecule by the

⁸ See Villars, D. S., *Chem. Rev.*, **11**, 369 (1932); Dennison, D. M., *Rev. Modern Physics*, **3**, 280 (1931).

⁹ Raman, C. V., and Krishnan, K. S., *Nature*, **121**, 501, 619 (1928); *Indian J. Physics*, **2**, 387 (1928); **6**, 263 (1931); *Trans. Faraday Soc.*, **25**, 781 (1929). The effect was independently discovered by Landsberg and Mandelstam, *Naturwiss.*, **16**, 557 (1928).

¹⁰ Dadiou, A., and Kohlrausch, K. W. F., *Ber.*, **63B**, 251 (1930); translation by Hollaender, A., *J. Opt. Soc. Am.*, **21**, 286 (1931). Hibben, J. H., "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, 1939.

absorption of visible or ultraviolet radations. The early development of the theory was due to Heurlinger, to Lenz¹¹ and to Kratzer.¹²

All lines accompanying a single given electronic transition belong to the same band system. The various bands within the system are ascribed to the accompanying vibrational transitions and the lines within the bands to the rotational shifts. Although but a few bands of the ground electronic state can be observed in infrared spectra, in the visible and ultraviolet band spectra a larger number of bands corresponding to quantum numbers as high as ten or twenty may be observed. In some cases it is possible to follow the asymptotic convergence of the successive bands toward a limit. This implies the gradual disappearance of the binding force between the atoms on increased separation during vibrations.

The considerations relating the various bands (taken from their zero lines) to each other are similar to those in the case of the infrared vibration-rotation spectra, and similarly, the structure of each band is analogous to that of the infrared band, a Q branch being also usually present. The close packing of the lines near the head of a band often makes it very difficult to disentangle the band structure. During the electronic shift there is a change in the structure of the molecule which involves a change in its moment of inertia.

Each line is given by an expression which involves a term for the contribution due to the electron shift, one for the vibration shift (together with a second power correcting term for the anharmonicity of the oscillator) and a term for the rotational shift together with a second power term introduced because of the change of the moment of inertia during the electronic shift. The structure of the band is thus given by $\nu = \nu_{0,1,0,0} + bm \pm cm^2$, in which b is approximately $h/4\pi^2 I$, the I referring to the lower electronic state. The constant c (about $0.1b$) may be positive or negative and corrects for the change in the moment of inertia. When negative, as m increases, it yields the R branch. As cm^2 grows faster than bm , the lines crowd together. At some value of m , cm^2 exceeds bm (the head of the band) so that with larger values of m there results a decreasing series with increasing spacings of the lines. The position of the head of the band depends on the ratio of b to c . When c is negative, the head occurs on the high frequency side of the origin. Negative values of m yield the P branch; these lines will gradually decrease in frequency and have greater separation as m increases. The intensities of the lines decrease and the band shades off on the lower frequency side. The Q branch lies between the R and P branches.

The complete interpretation of the band spectrum of a compound is a matter of great difficulty largely because of the great number of energy states which may be possessed by a molecule. Even the classification of the lines into the bands, series of bands, and electronic band systems is rendered very difficult because of overlapping of the various structural units and because the electronic energy states, like those of atomic spectra, exhibit multiplicity. The early development of the theory¹³ was based upon a formal analogy between line and band spectra, the electronic terms of each involving various quantum numbers; similar selection principles were used. The systematization of the relations between the electronic structures of diatomic molecules and the nature of their band spectra is due in large part to Mulliken,¹⁴ who proposed a notation for designating the state of each electron and of the molecule as a whole.¹⁵

¹¹ Lenz, W., *Verh. deutsch. Phys. Ges.*, **21**, 632 (1919).

¹² Kratzer, A., *Ann. Phys.*, **67**, 127 (1922); **71**, 72 (1923).

¹³ Mecke, R., *Physik. Z.*, **26**, 217 (1925); *Z. Physik*, **28**, 261 (1924); **32**, 823 (1925); **31**, 709 (1925); **36**, 795 (1926); *Naturwiss.*, **13**, 698 (1925). Hund, F., *Z. Physik*, **36**, 657 (1926); **51**, 759 (1928); Birge, R. T., *Nature*, **117**, 300 (1926).

¹⁴ Mulliken, R. S., *Proc. Nat. Acad. Sci.*, **12**, 144, 151 (1926); *Phys. Rev.*, **29**, 391, 921 (1927); **30**, 138, 150, 175, 785 (1927); **32**, 186, 761 (1928); **33**, 730 (1929).

¹⁵ Other important contributions were made by Birge, R. T., *Phys. Rev.*, **27**, 245 (1926); Kemble, E. C., *Z. Physik*, **35**, 286 (1925); *Proc. Nat. Acad. Sci.*, **10**, 274 (1924); *Phys. Rev.*, **25**, 1 (1925); Kratzer, A., *Z. Physik*, **33**, 144 (1925). The subject is one for a specialist.

In analogy with the S, P, D. . . . terms for atoms there are recognized Σ , Π , Δ terms for molecules. These correspond to the successive values of a quantum number Λ (0, 1, 2). While in the atom, the orbital number L gives the resultant orbital angular momentum of all the electrons, in the molecule the presence of the two nuclei introduces certain complications. But, since the internuclear line is still an axis of symmetry, the component of the orbital angular momentum along this line remains a constant, which may be measured in units of $h/2\pi$. As in the case of the atom, the resultant spin angular momentum of all the electrons serves as another quantum number S . Dependent upon its value (0, $\frac{1}{2}$, 1 . . .) there may be singlet, doublet, triplet states of the molecule. The multiplicity is given by $2S+1$ and is denoted in writing a term by an upper left-hand index before the term symbol, which is derived from the value of Λ . The $^2\Sigma$ represents a state with $\Lambda=0$, $S=\frac{1}{2}$, a $^1\Pi$ term a state with $\Lambda=1$, $S=0$, and a $^3\Delta$ term a state with $\Lambda=2$, $S=1$. As with atoms, S is integral or half-integral depending on whether the total number of electrons in the molecule is even or odd. The multiplicity is even for uneven electron numbers and uneven for even electrons. Other features of term designations may be found in specialized treatises.

It is unnecessary to discuss here the various selection principles which have been given to account for the relative frequencies of the transitions between various molecular energy states. Much is known in regard to the lives of the excited states, but the methods by which these may be calculated by means of the Schrödinger equations are primarily of interest to the specialist. For electron transitions in the wave-number range 10^4 - 10^5 cm^{-1} , the excited states have a life of about 10^{-8} second. For transitions in vibration frequencies in the range of 10^2 - 10^3 cm^{-1} the life of the excited states is of the order of 0.01 second. The lives of rotational states may be even longer.

Account must also be taken of the existence of the spins of the nuclei, information about which is yielded by studies of the alternating intensities of the lines in a band of a homopolar molecule.¹⁶ If the two spins oppose each other, the molecule is called symmetrical and if they are in the same direction, it is called antisymmetrical. Wave mechanics indicates the probability of the existence of antisymmetrical hydrogen to be three times that of symmetrical hydrogen. Ordinary hydrogen behaves as a mixture of two gases. The discovery of the existence of this mixture was a spectacular outcome of the work on band spectra. At very low temperatures all of the hydrogen is in the symmetrical form. Bonhoeffer and Harteck have found charcoal to act as a catalyst for the conversion of one form to the other. The two forms have different specific heats and the change in the proportion of the two effected in the presence of the catalyst can be demonstrated by a change in the heat conductance. The antisymmetrical form has been denoted ortho- and the symmetrical form as para-hydrogen. In hydrogen at room temperatures, there is three times as much ortho- as para-hydrogen. The existence of these two forms of hydrogen was predicted by Heisenberg¹⁷ and by Hund.¹⁸ Bonhoeffer and Harteck later made detailed studies of the physical properties of the two forms.¹⁹ Adsorption on charcoal at liquid air temperatures gives practically pure para-hydrogen.

¹⁶ Mulliken, R. S., *Trans. Faraday Soc.*, **25**, 634 (1929).

¹⁷ Heisenberg, W., *Z. Physik*, **41**, 239 (1927).

¹⁸ Hund, F., *Z. Physik*, **42**, 93 (1928); see also Dennison, D. M., *Proc. Roy. Soc.*, **115**, 483 (1927).

¹⁹ Bonhoeffer, K. F., and Harteck, P., *Naturwiss.*, **17**, 182, 321 (1929); *Z. physik. Chem.*, **4B**, 113 (1929); **5B**, 292 (1929); see also Eucken, A., and Hiller, K., *Ibid.*, **4B**, 142 (1929).

Isotopes in Band Spectra. Since different isotopes of an element have different masses, the momenta of inertia of molecules containing different isotopes should be different. As a result, the bands in the visible or ultraviolet due to molecules some of which have one and others another isotope will be characterized by a duplication of the lines. The bands themselves are also split and superposed.

The existence of isotopes of carbon (13), nitrogen (15), oxygen (17) and of certain other elements were predicted from the data of spectroscopy before they were found by the use of the mass spectrograph of Aston. The oxygen isotope (18) was detected in this manner by Giauque and Johnston in 1929. In the electronic band spectra of isotope mixtures, there is a splitting of the zero position of the bands due to an electronic shift between "vibrationless" states. Its existence implies that the "non-vibrating" molecule is actually in vibration since two isotopic molecules in this state are energetically different. The occurrence of this phenomenon makes certain the existence of a "zero-point" energy of vibration and accounts for the use of $(v + \frac{1}{2})$ in the succession of vibrational terms used in the formulas for the zero lines of bands.

Attempts have been made to effect a separation of isotopes by photochemical means. Kuhn and Martin²⁰ irradiated phosgene with monochromatic light (2816.179A) obtained from an aluminum arc by the use of filters, and found that the liberated chlorine showed a slight excess of Cl³⁵. Zuber²¹ effected a partial separation of the isotopes of mercury by photooxidation by the aid of a filter which transmitted only the hyperfine components of a spectral line capable of exciting only certain isotopes.

This brief review of the nature and structure of molecular spectra is intended only to serve as an indication of their importance in yielding data of fundamental significance to many branches of chemistry. In the detailed discussion of photochemical reactions in the remainder of the book we shall be concerned with molecular spectra only in so far as they yield information regarding the stability of a photochemically reacting molecule. When by the absorption of energy a molecule is raised to successively higher and higher vibrational states, it may be made to dissociate when the requisite amount of energy has been absorbed. Usually, however, for a vibrational state producing dissociation to be obtained by a molecule absorbing in its ground state, quanta great enough to produce an electronic transition are required. The electron shift alters the binding of the atoms in such a manner that the excited molecule upon the simultaneous acquisition of the requisite amount of energy may be raised to a vibrational state which leads to its dissociation. This is the most frequently occurring primary process in photochemical reactions. The applications of band spectral data to the interpretation of photochemical processes will be considered in more detail in the following chapter.

The following are sources of information on band spectra for readers desirous of obtaining a more thorough discussion, including the mathematical treatment, of band spectra.

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²⁰ Kuhn, W., and Martin, H., *Naturwiss.*, 20, 772 (1932); *Z. physik. Chem.* 21B, 93 (1933).

²¹ Zuber, K., *Nature*, 136, 796 (1935); *Helv. Phys. Acta*, 9, 285 (1936).

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Chapter 14

Spectroscopic Evidence for Dissociation as the Primary Photochemical Process

It is now necessary to consider the manner in which the stability of a molecule sets a limit to the amount of vibrational energy which it can absorb and still remain a molecule. The guiding principle is that a molecule either in the ground state or, as is more commonly the case, in one of its electronically excited states, cannot absorb more vibrational energy than corresponds to its work of dissociation without falling apart into atoms or, if it is a polyatomic molecule, into atoms and free radicals, or two free radicals.

The present viewpoint may be said to have taken its origin from the work of Franck on the dissociation of molecules by electron impact. Blackett and Franck¹ found experimentally that a hydrogen molecule can be decomposed by one collision, a continuous spectrum appearing at the same time. They suggested that the first effect of the collision is to raise an electron suddenly to a higher level. In this new configuration there is a large repulsion between the nuclei great enough to split the molecule into a normal atom and an excited one, both atoms having high velocity. Franck² extended the concepts derived from these experiments to an interpretation of photochemical dissociation. In this case the excitation of the molecule and its resultant dissociation are produced, not by a collision with a rapidly moving electron, but the absorption of a quantum $h\nu$ equal to or greater than the work of dissociation of the molecule. If the separation of the atoms during a vibration becomes great enough to overcome the binding force between the nuclei, the atoms may fall apart. It was, however, well known that quantities of energy larger than the work of dissociation may be absorbed by molecules without destroying them. Franck explained this by showing that in such cases not all of the absorbed energy is available as vibrational energy. Instead, a large part of the absorbed energy is consumed in raising the electron system to a higher quantum state, the remaining energy being available only for changing the vibrational and rotational states. Since the rotational quantum is but small, the effects of a change in rotational energy may be neglected. The problem may thus be reduced to that of the stability of the molecule in its various electronically excited states with respect to vibrational energy. Franck prepared potential energy diagrams in which the potential energies of the vibrating atoms are plotted as ordinates against the separation of the atoms as abscissae. Before considering these curves and their relation to spectroscopy, it may be simpler to consider the manner in which molecular spectra indicate the occurrence of dissociation.

INTERPRETATIONS OF CONTINUOUS REGIONS IN SPECTRA

In Chapter 2, it was stated that in atomic spectra the lines of a series converge to a limit. On the short-wave side of this limit the spectrum is continuous. This

¹ Blackett, P. M. S., and Franck, J., *Z. Physik*, **34**, 389 (1925).

² Franck, J., *Trans. Faraday Soc.*, **21**, 536 (1926).

was interpreted as indicating the separation of an electron from an atom, the latter thereby becoming an ion. The absorption is continuous rather than discrete because the motion of the electron on leaving the atom is not quantized. The velocities with which the electrons are ejected from the various atoms present in the absorbing gas vary continuously and are not limited to definite values. Non-quantized energy levels correspond to non-periodic movements. During the process of ionization the electron changes its motion from a periodic one in an orbit to a non-periodic one in the hyperbolic path which carries it away from the ion. When at a sufficient distance from the ion the electron moves in practically a straight line. It may have any kinetic energy depending upon the amount by which the particular wave-length absorbed exceeded in energy the amount required for the ionization. Since in the light producing the ionization there may be present quanta varying almost continuously in magnitude, atoms absorbing any quantum, A , more than sufficient to produce ionization, will give kinetic energy to the electrons and the ions corresponding to the excess energy. But atoms ionized by quanta corresponding to a wave-length infinitesimally near to that corresponding to A will produce electrons having an infinitesimally greater kinetic energy. Thus when a wave-length band of energy greater than that required to produce ionization is absorbed, the electrons produced will be endowed with continuously varying kinetic energies. Thus it is that in atomic line spectra a continuous region beginning at the convergence limit of a series marks the frequency which corresponds to the work of ionization.

A similar ionization of a diatomic molecule can occur but is rarely of photochemical significance. Before ionization of the molecule could be attained, the energies required would be usually more than sufficient to break the molecule into atoms. The effect of dissociation upon the appearance of the spectrum is, however, similar to that of ionization.

Before dissociation, the atoms of a molecule are vibrating to and fro on the line joining their nuclei. With increasing increments of vibrational energy they are separated more and more widely at each oscillation. When the separation becomes great enough the restoring force between the atoms becomes reduced to zero, the vibratory motion between the atoms ceases, and the atoms become separated. Since the kinetic energies with which the atoms move are not quantized, the absorption spectrum becomes continuous at wave-lengths shorter than that which corresponds energetically to dissociation. It must be noted that the molecule which dissociates rarely is in its ground electronic state. Therefore, the energy of dissociation need not be expected to coincide with that required for thermal dissociation. The wave-length at which the spectrum becomes continuous represents the convergence limit of a series of vibrational states of the dissociating molecule in the electronic state from which dissociation occurs. Dymond³ found a continuous range in the absorption spectrum of iodine vapor. Bonhoeffer and Steiner,⁴ as well as Tingey and Gerke,⁵ reported a continuous region in the absorption spectrum of hydriodic acid.⁶

Corroboratory evidence for the theory that a region of continuous absorption implies dissociation was soon forthcoming from measurements of the fluorescence of vapors at low pressures. It was stated in Chapter 12 that when the pressure is low, so that collisions are rare, excited molecules re-emit their excitation energy

³ Dymond, E. G., *Z. Physik*, **34**, 553 (1925).

⁴ Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926).

⁵ Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926).

⁶ See also Leifson, S. W., *Astrophys. J.*, **43**, 73 (1926), for other gases.

as fluorescence after a period of about 10^{-8} second. Dymond,⁷ observed this fluorescence in iodine vapor excited by the absorption of long wave-lengths. But when the absorbed light had only wave-lengths less than about 5000Å, the region in which continuous absorption begins, this fluorescence could no longer be observed, an indication that the molecules were no longer present and so could not reemit their energy of excitation. Similar observations were reported by Bonhoeffer and Farkas.⁸ The fluorescence test for dissociation is limited to very low pressures of gas or vapor, since when the pressure is high deactivating collisions become frequent and might remove the excitation energy and so extinguish fluorescence even though dissociation by direct absorption did not occur. Errors due to the emission of radiation as a result of the recombination of atoms to form molecules rarely arise, since, as has been noted in Chapter 13, free atoms rarely combine to form molecules with the emission of their excess energy.⁹

Other types of experimental evidence have been advanced to support the theory of direct dissociation. One method employs identification of the resulting free atoms by their characteristic absorption lines. Iodine atoms absorb the 1830.4Å line strongly, but iodine molecules do not. Turner found that iodine vapor when irradiated by a carbon arc shows an increased absorption of this line, indicating the presence of iodine atoms. Senftleben¹⁰ demonstrated that excited mercury atoms can dissociate hydrogen. The dissociation was measured by change in the heat conductivity of the gas by a method dependent upon a change in resistance of a wire kept in the gas. With Germer, he extended the method to show the direct dissociation of the halogens on irradiation. That the energy absorbed in excess of that required for dissociation appears as kinetic energy of the atoms was demonstrated by Hogness and Franck¹¹ for the case of sodium iodide vapor at 650°C. The dissociation yields a normal iodine atom and an excited sodium atom, the latter spontaneously emitting the sodium D line. The Doppler effect (shift in wave-length of the light from a moving source) was utilized to secure information as to the kinetic energy of the sodium atom when produced by the dissociation of the sodium iodide vapor by various wave-lengths within the region of continuous absorption. The Doppler effect was measured by the relative transmission of the emitted light by a layer of sodium vapor, which can only absorb the D line. When the dissociation was effected by a silver arc giving effective intense radiation only in the neighborhood of 2450Å, 80 per cent of the emitted light was absorbed by sodium vapor. When the dissociating source was a cadmium arc emitting shorter wave-lengths (capable of giving more kinetic energy to the dissociated atoms), only 76 per cent of the emitted light was absorbed by the sodium vapor. With the still shorter radiations of a zinc arc (2139-2026Å), the Doppler effect was increased to such an extent that but 50 per cent of the emitted light was absorbed. In this way it could be shown that the kinetic energy of the liberated atoms increases as the frequency of the irradiating light is increased beyond a limit corresponding to 2450Å.

Polyatomic molecules, as water, methanol and methyl cyanide, when decomposed by radiations within the Schumann region give rise to excited free radicals, such as OH and CH, which spontaneously emit characteristic bands.¹² Still

⁷ Dymond, E. G., *loc. cit.*

⁸ Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

⁹ Kondratjew, V., and Leipunskii, A., *Z. Physik*, **50**, 366 (1928); **56**, 353 (1929); *Trans. Faraday Soc.*, **25**, 736 (1929).

¹⁰ Senftleben, H., *Z. Physik*, **32**, 922 (1925).

¹¹ Hogness, T. R., and Franck, J., *Z. Physik*, **44**, 26 (1927).

¹² Terebin, A., and Neufmin, H., *Nature*, **134**, 255 (1934).

other lines of direct evidence for the liberation of free atoms and free radicals, such as the conversion of para-hydrogen to ortho-hydrogen, and the effects of free radicals on metallic films, have been advanced. There is now general agreement that photodissociation in a single act of absorption may occur as a result of a primary absorption process. In the case of the reactions of gases which contain a small number of atoms, the nature of the absorption curve of the gas affords a reliable criterion for the occurrence of dissociation. When the absorption lies within a continuous region, the result is dissociation. In the case of very complex gaseous molecules containing more than about six atoms, the evidence from spectroscopy is less definite, since the banded region is not well marked in their spectra. In reactions conducted in solution, absorption curves afford little or no evidence regarding the nature of the primary process. (See Chapter 20.)

FRANCK'S POTENTIAL ENERGY CURVES

In his Faraday Society paper, Franck visualized the distinction between the dissociation of excited states of molecules and their stability in the ground state by the aid of the potential energy diagrams reproduced in Figure 106. In each

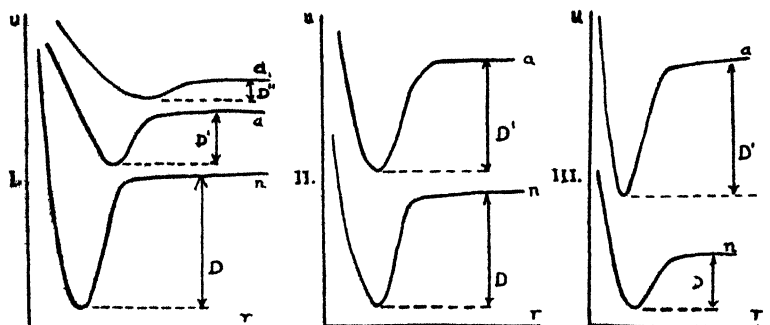


FIGURE 106. Potential Energy Diagrams of Franck (*Transactions of the Faraday Society*).

of the three diagrams, the lower curve applies to the ground state of a molecule and the upper curve or curves to various electronically excited states. The differences between the upper and lower curves are intended to illustrate the manner in which the change in electron configuration alters the stability of the molecules. To understand the nature of a single one of these curves, it is simplest to consider first the discussion of the meaning of the curves as described by Rabinowitsch in a paper on the interpretation of band spectra.¹³

It was stated in Chapter 13 that for the pure harmonic oscillator,

$$K = -az$$

This means that the restoring force during an harmonic oscillation is proportional to the displacement z on either side of an equilibrium separation of the atoms of a diatomic molecule. Integration yields the potential energy:

$$P = \frac{az^2}{2}$$

¹³ Rabinowitsch, E., *Z. Elektrochem.*, **37**, 91, 370 (1931).

This is the equation of a parabola (Figure 107) with its two branches meeting at $x=0$, the equilibrium distance between the nuclei, r_0 , being measured from the origin. During a vibration from the point of greatest separation of the atoms, the potential energy follows the course of the curve. When the atoms are far apart the attractive forces of valence require that there be a great potential energy. As they move toward each other, this becomes transformed into kinetic energy. At the equilibrium point the potential energy is zero, all the energy being kinetic. As the kinetic energy carries the atoms closer together, the energy again becomes potential because the repulsive forces of the nuclei tend to keep the atoms from coming together. The position of equilibrium (determined as described in the previous chapter from rotational term separations) depends upon the relative magnitudes of the attractive and repulsive forces of the atoms. If the molecule possesses energy denoted by A on the ordinate, a line parallel to the abscissa

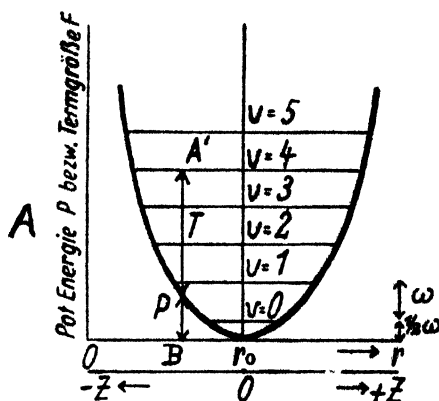
FIGURE 107.

Potential Curve and Vibrational Terms for Harmonic Vibrator (Rabinowitsch, *Z. Electrochemie*).

Z = Elongation

r = nuclear separation

$Z = r - r_0$



drawn through A would cut the curve in two places. These determine the distances between the atoms at the extremes of its vibrations when it possesses this amount of potential energy. At these distances from the equilibrium position the total energy of the molecule is potential; there is no kinetic energy. The atoms, changing their directions, are momentarily at rest with respect to each other. At any other distance between the atoms, as for example, at A' , part of the energy is potential and part kinetic. By dropping a perpendicular from this point to the abscissa, it is evident that the relative fraction which is potential is given by the ratio $BP:BA'$. Since the vibrational states of the molecule are quantized, the potential energies of the molecule in its permitted states are obtained by drawing a series of equally spaced lines parallel to the abscissa. The extremes of separation of the atoms in each of these vibrational states are given by the points at which each of these lines cuts the curve. The equal spacing of the lines corresponds to successive integral quantum numbers.

It is to be especially noted that the first of these, the so-called "vibrationless state" is so drawn as to indicate that even in it the molecule is vibrating with one-half the energy corresponding to its fundamental frequency. It may be recalled that account was taken of this "zero-point energy" in the equation for expressing the wave numbers of vibration band zero lines in terms of a transition between states. (Chapter 13.)

Since real molecules are not harmonic oscillators, certain changes must be made in the form of the potential energy curve, which nevertheless retains its parabolic form near the equilibrium point. The value of x , the anharmonicity factor in the expression for a vibrational term $F_v = (v + \frac{1}{2})\omega - (v + \frac{1}{2})^2 x\omega$ yields the deviation from the ideal curve to a first approximation. The deviations really result from the necessity for the use of terms in higher powers in the expression for the force of attraction of the oscillator. The effects of the deviations from harmonic oscillations are such as to make the repulsive forces increase more rapidly than linearly as the atoms approach each other, so that the left branch of the curve must be steeper than that of a true parabola. The attractive force no longer increases regularly with the separation. Instead, it attains a maximum at a certain distance of separation of the atoms, after which it becomes smaller and the right-hand branch of the curve changes direction, and finally, at a certain separation of the atoms asymptotically becomes parallel to the abscissa. (See the lower curves of Figure 106.) This means that the atoms no longer attract each other, so that, after attaining a certain separation, they may move away from each other independently and the molecule is dissociated. The value of the energy at which the curve becomes horizontal represents the energy required for dissociation.

In the schematic curves drawn by Franck to illustrate the behavior of various hypothetical molecules (Fig. 106), a deep curve such as I (normal), represents a stable molecule, since the dissociation energy is great. One such as III n is not nearly so stable, since the dissociation energy is less. The minima for the curves of the excited molecules are situated at heights which represent the electronic (and rotational) energies of the non-vibrating electronic states. The energy for the dissociation of the excited molecules is measured only from the potential energy of their minima. To dissociate such an excited molecule photochemically would require in addition to this energy, the energy required to form the excited state from the original ground state.

The various curves illustrate the fact that the excitation of a molecule may either weaken, strengthen or leave unchanged the binding strength of the atoms in the ground state. In I, which shows curves for a molecule in its ground state and in two excited states, a, a' , the excitation progressively weakens the binding force. Not only does the energy of dissociation lessen, but since the attractive force is weakened, the separation of the atoms at equilibrium also becomes progressively greater with successive states of excitation. Should the absorption of light which produces the electron transition be represented by drawing a vertical line upwards from the minimum of the curve for the ground state, it would strike the curve for the first excited state at a point indicating a potential energy greater than that (D') required to dissociate the excited molecule. Its atoms would, therefore, fly apart as the vibration traced the curve for the excited state. This type of molecule is encountered in the halogens.

The second part of the figure illustrates the case in which the strength of the binding is independent of the state of excitation.

Section III indicates the case in which the binding is made firmer by excitation, so that the moment of inertia is reduced. Examples are such loosely bound molecules as Cd_2 or Zn_2 for which the heat of dissociation is of the order of less than one kcal.¹⁴

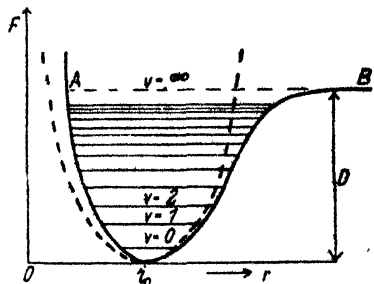
If in such potential energy curves, the horizontal energy levels for the terms

* Winans, J. G., *Nature*, 123, 279 (1929); *Phil. Mag.*, 7, 555 (1929).

corresponding to the successive quantum numbers are drawn in, as in Figure 107 for the harmonic oscillator, the first two or three would be widely and approximately equally spaced. But with successively higher quantum numbers, they become more and more closely spaced (Figure 108), eventually converging at the level at which dissociation occurs. In comparatively few molecular spectra, notably chlorine and iodine, is it possible to trace the convergence of a large number of bands to a limiting frequency which indicates a heat of dissociation.

FIGURE 108.

Potential Curve and Vibrational Terms for Anharmonic Vibrations (Rabinowitsch, *Z. Elektrochemie*).



In most cases, the bands become weak while still far from the convergence limit and only a limited number of the vibration quanta can be measured directly. Birge and Sponer¹⁵ devised a method of extrapolation to obtain the convergence point.

From the separations of two or more bands, $\Delta\nu = \omega_0(1 - 2\nu x)$ it is possible to derive values of the fundamental frequency of the molecule ω_0 and of its anharmonicity x . From these, it was believed that all higher terms might be obtained on the assumption that $\Delta\nu$ is a linear function of ν , decreasing as the quantum number increases. At the convergence limit, where $\Delta\nu$ is zero, ν is given by $1/2x$. The total energy absorbed is then the integral of ΔF_v between the limits $\nu = 0$ and $\nu = 1/2x$ or $\omega/4x - \omega/2$. To this there must be added the zero-point energy $\omega/2$, so that the heat of dissociation would be equal

to $\frac{h\nu}{4x}$. For a graphical solution, $\Delta\nu$ could be plotted against ν and extrapolated to $\Delta\nu = 0$, that is to $\nu = 1/2x$, the area under the curve giving the heat of dissociation.

Application of this method gave results for the heat of dissociation which in many cases were far too high in comparison with values obtained from thermochemical data. It came to be recognized that the equations employed were not strictly valid and that the results were frequently uncertain when but few vibrational bands could be measured and employed in the extrapolation. Near dissociation, the drop in the separation of the vibrational bands often seemed to be accelerated. Birge¹⁶ modified the extrapolation methods. In the method suggested by Birge, ω_0 is plotted against the energy of vibration. $E\omega_0 = \Sigma\omega_n$. By the use of the improved method the following values for the heats of dissociation of various gases (expressed as electron-volts) were obtained: N₂ 9.1, O₂ 6.0, NO 6.6, CO 10.3¹⁷

Although Franck said little in his Faraday Society paper as to the manner in which the potential energy curves were obtained, the fertility of the concepts they expressed and their value in the interpretation of the various types of photochemical mechanism were quickly appreciated. Condon¹⁸ devised methods of

¹⁵ Birge, R. T., and Sponer, H., *Phys. Rev.*, **28**, 259 (1926). Other methods of evaluating heats of dissociation from the long-wave limits of continuous spectra and from predissociation spectra are occasionally employed but cannot be discussed here.

¹⁶ Birge, R. T., *Trans. Faraday Soc.*, **25**, 707 (1929).

¹⁷ For the application of the Birge-Sponer method to the determination of the heats of dissociation of organic compounds from their infrared absorption curves, see Ellis, J. W., *Phys. Rev.*, **33**, 27 (1929).

¹⁸ Condon, E. U., *Phys. Rev.*, **28**, 1182 (1926); **32**, 858 (1928); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927).

treating the curves more quantitatively from the standpoint of quantum mechanics and used them in explaining the distribution of the intensities of the lines encountered in band spectra. He conceived an electron transition to occur with such extreme rapidity that the light electron moves to its new orbit in a time so brief that the heavier and more slowly moving nuclei undergo practically no change in position or velocity during the transition. This may be indicated by drawing a vertical line joining the curves for the ground and excited states of the molecule. The transitions occur with the greatest probability from the end points of greatest extension and compression of the molecule where the velocities of the atoms are least. Accordingly the bands corresponding to transitions from the points of reversal of the vibration have the greatest intensity. Strictly the method is not exact since the Heisenberg uncertainty principle shows that it is impossible to know simultaneously the positions and velocities of the nuclei. The error introduced is, however, eliminated by treatment by the methods of wave mechanics.

If the vertical cuts the curve for the excited molecule at a point deeper than its horizontal asymptote, the absorption spectrum will be predominantly banded, since vibration is possible. But if the curve for the excited state be cut at a point corresponding to a potential energy greater than that of the asymptote, the absorption will be predominantly continuous.¹⁹ It must be noted that there may be several excited states for which separate curves must be constructed.

It is possible to derive the shape of the Franck-Condon curve for a diatomic molecule from a knowledge of three constants of the molecule, r_0 , ω and D by means of an interpolation formula due to Morse,²⁰

$$F = D'e^{-2ax} - 2D'e^{-ax}$$

in which $a = \sqrt{\frac{8\pi^2 c \mu \omega x}{h}} = 0.2454 \sqrt{M \omega x}$, μ being the reduced mass in c.g.s. units

and M its value in atomic weight units; x is the elongation or the distance from the normal equilibrium nuclear separation r_0 , the value of which for a given vibrational quantum number is derived from an analysis of the band spectrum. D' is the heat of dissociation derived thermochemically or by a Birge-Sponer extrapolation.²¹ Such curves have been obtained for a large number of molecules and the curves play an essential role in theories regarding thermal reaction rates.²²

Despite the many difficulties inherent in treating polyatomic molecules, Franck, Sponer and Teller²³ believe that potential energy curves may be profitably employed, at least in qualitative discussions of predissociation.

EXCITED ATOMS FORMED BY DISSOCIATION

Early efforts to test the dissociation theory by comparing the heats of dissociation determined spectroscopically and thermochemically indicated discrepancies; these for a time led certain workers to prefer the theory that the primary process in a photochemical change is more generally one of molecular excitation.

¹⁹ For quantum mechanical treatments, see Goldstein, L., *Compt. rend.*, **193**, 919 (1931); *J. phys. Radium*, **4**, 123 (1933).

²⁰ Morse, P. M., *Phys. Rev.*, **34**, 57 (1929).

²¹ The calculation of such curves has also been described by Klein, O., *Z. physik*, **76**, 226 (1932). Improved methods have been suggested by others, for which see Sponer, H., "Molekülspektren," J. Springer, Berlin, 1936. Note also Chakravorti, S. K., *Z. Physik*, **109**, 25 (1938).

²² For further discussion of potential energy curves, see Franck, J., and Sponer, H., *Nachr. Ges. Wiss. Göttingen*, **241** (1928); Visser, G. H., *Chem. Weekblad*, **27**, 237, 380, 390 (1930); Mecke, R., *Physikal. Z.*, **33**, 1 (1932); Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 280 (1933); Rüdý, R., *Rev. gen. sci.*, **37**, 539 (1926); Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927); Suguiera, J., *Ibid.*, **45**, 484 (1927); Hylleraas, E., *Ibid.*, **96**, 643 (1935); Finkelburg, W., *Ibid.*, **99**, 798 (1936).

²³ Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

That the atoms formed on dissociation of a molecule need not be in the ground state, but that either one or both might be liberated in an excited state was discussed by Franck. If such should be the case it is evident that the apparent value of the heat of dissociation would be greater than the thermochemical value by the energy of excitation. If then the state of excitation of an atom so formed can be determined and if the energy required to raise the atom to that state from the ground state be known, it should be possible to obtain the heat of dissociation from the ground state of the molecule by subtracting the heat of excitation of the atom from the spectroscopic value for the heat of dissociation of the excited molecule.

Iodine may absorb nearly double its dissociation energy and re-emit it as fluorescence without dissociating. From spectroscopic data of Mecke,²⁴ Franck stated the convergence limit of the vibrational levels of iodine to lie at 4995A. Figure 103 shows that this corresponds to 56,950 calories. Since the thermochemical value for the heat of dissociation of iodine is only 34,500 calories, it is evident that some other process than dissociation of the ground state must be involved in the photochemical dissociation. From the arc spectrum of the iodine atom, its energy of excitation to the $^2P_{1/2}$ state is found to be 21,650 calories per atom. When this is deducted from 56,950 calories, the remainder, 35,300 cal.,²⁵ is in good agreement with the thermochemical value. The conclusion is, therefore, that the photochemical dissociation of iodine leads to the production of one normal and one excited atom. Similarly, the convergence limit is 4800A for chlorine and for bromine 5107A, each dissociating into a normal and an excited atom.

A normal molecule rarely suffers photochemical dissociation; when it does two normal atoms usually are formed. Herzberg²⁶ and Heitler and Herzberg²⁷ have shown that there are instances in which molecules may yield one normal and one excited atom from the ground state, and two normal atoms from an excited state. This is interpreted to mean that a stable molecule is formed by the union of a normal and an excited atom. Instances are CN, BO, SiN, N_2^+ , $(CO)^+$. Still other cases have been discussed by Bengtsson and Hulthén, *e.g.*, CuH.²⁸

HOMOPOLAR AND HETEROPOLAR MOLECULES

Molecules which, like the alkali halides, yield ions on dissociation from the ground state are called heteropolar or ion-molecules, and those which yield two neutral atoms from the ground state are called homopolar or atom-molecules. In general, atom-molecules such as hydrogen, chlorine, and even such polar ones as silver halides are dissociated from excited states into a normal and an excited atom. Ion-molecules may give both this type of dissociation and one in which only normal state atoms are produced.²⁹ Franck, Kuhn and Rollefson³⁰ found the alkali halide vapors to exhibit continuous absorption bands which extend farther toward the red when the temperature and pressure are increased; the position of the maximum absorptions appeared to be independent of these factors. Only one maximum was observed for the chlorides, but there were two for the iodides and bromides. The heats of dissociation of the molecules as calculated from the

²⁴ Mecke, R., *Ann. Physik*, **71**, 104 (1924).

²⁵ 35,593 according to Brown, W. G., *Phys. Rev.*, **38**, 709 (1931).

²⁶ Herzberg, G., *Ann. Physik*, **86**, 189 (1928).

²⁷ Heitler, W., and Herzberg, G., *Z. Physik*, **53**, 52 (1929).

²⁸ Bengtsson, E., and Hulthén, E., *Trans. Faraday Soc.*, **25**, 751 (1929).

²⁹ Sponer, H., *Z. Elektrochem.*, **34**, 483 (1928); Franck, J., and Kuhn, H., *Naturwiss.*, **20**, 923 (1932).

³⁰ Franck, J., Kuhn, H., and Rollefson, G. K., *Z. Physik*, **43**, 155 (1927).

positions of the longer wave-length continuous bands appeared to be in agreement with thermal heats of dissociation of the salts. Such a conclusion would indicate that it would be possible for ion molecules to be dissociated into two normal atoms.

At low pressures, the vapor of sodium iodide when irradiated with wave-lengths shorter than 2500A emits the D line of sodium.⁸¹ This is proof that the absorption produces an excited sodium atom and an iodine atom. The second series member 3303A only appears when the iodide vapor is irradiated with the 1854-62A aluminum doublet, the energy corresponding to the dissociation energy of the sodium iodide and the excitation of the sodium atom to the 3P state. Since in this process the D line was not emitted, it is not possible that the effects could have been due to an ionization of some sodium vapor possibly present.⁸² Similar results were reported by Kondrat'ev⁸³ for caesium iodide, the dissociation energy of which corresponds to 3.82 volts. The energy required to excite the observed caesium line (4555A) is 2.71 volts. The sum, 6.53 volts, is less than the energy of the aluminum lines 1854 and 1862A which produce the effect, but greater than that of the nickel lines about 2300A, which are ineffective.

In thallium iodide vapor, irradiation with wave-lengths shorter than 2080A leads to the emission of the 3776 and 5351A lines, showing that the dissociation produces thallium in the 2S state; from the result the heat of dissociation into normal atoms would be 61 kcal. per mole.⁸⁴ More recently, Terenin and Popov⁸⁵ find thallium iodide and bromide to yield thallium and halide ions. Butkov,⁸⁶ had previously stated from convergence limits, the heat of dissociation of thallous chloride vapor as 87 kcal. and that of the bromide as 73.1 kcal. Since the decomposition leads to excited atoms, the vapors are atomic compounds.

Neuimin⁸⁷ finds thallous iodide at 600° and 1 mm. pressure to show two absorption bands with maxima at 3110 and 2510A, diffuse toward the long wave side, corresponding to the potential energy curves for $Tl + Cl^*$ and $Tl^* + Cl$. On irradiating these vapors at 100 mm. by a spark, the photodissociation of the salt yields the lines 3776 and 5351A. These atomic lines are not given by resonance in thallium vapors at these temperatures.⁸⁸

Desai⁸⁹ found four regions of continuous absorption to be exhibited by the vapors of rubidium iodide. The first, at 3700A, involves a dissociation into normal atoms with an energy of reaction of 78 kcal. The second at 2900A, leads to the production of a normal rubidium and an excited iodine atom, the third at 2548A, to an excited rubidium and a normal iodine atom, and the fourth at 2150A, to the formation of excited rubidium and iodine atoms.⁴⁰

Sommermeyer⁴¹ agrees that the absorption of alkali halide vapors yields only continuous spectra, but finds that by an excitation method he can observe certain

⁸¹ Kondrat'ev, V., *Z. Physik*, **39**, 191 (1926); Terenin, A., *Ibid.*, **37**, 98 (1926); **44**, 713 (1927); *Naturwiss.*, **15**, 73 (1927).

⁸² See also Terenin, A., and Neuimin, H., *Physik. Z. Sowjetunion*, **2**, 434 (1932).

⁸³ Kondrat'ev, V., *loc. cit.*

⁸⁴ Terenin, A., *Z. Physik*, **44**, 713 (1927).

⁸⁵ Terenin, A., and Popov, B., *Z. Physik*, **75**, 338 (1932).

⁸⁶ Butkov, K., *Z. Physik*, **58**, 232 (1929).

⁸⁷ Neuimin, H., *J. Exp. Theor. Physics, U.S.S.R.*, **4**, 692, 697 (1934); see also Terenin, A., and Popov, B., *Z. Physik*, **75**, 338 (1932).

⁸⁸ See also Franck, J. M., *Physik. Z. Sowj.*, **2**, 319 (1932).

⁸⁹ Desai, M. S., *Z. Physik*, **85**, 360 (1933).

⁴⁰ See also Visser, G. H., and van Heel, A. C. S., *Z. Physik*, **86**, 694 (1933). For alkali fluorides and the heat of dissociation of fluorine, see Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **1**, 116 (1931-2); *Chem. Abs.*, **26**, 5842 (1932).

⁴¹ Sommermeyer, K., *Naturwiss.*, **16**, 653 (1928); *Z. Physik*, **56**, 548 (1929).

bands. Their separation was less at the longer wave-lengths and in the ultra-violet they became progressively feebler and finally disappeared. They correspond with the vibration quantum of the normal state of the molecule, which would be strongly excited at the temperatures used (750°). He suggested that the normal electronic state always corresponded with ionic binding, and the excited state with binding by polarization.

The absorption of lithium halide vapors has been studied by Desai⁴² who found two absorption regions in the vapors of the bromide and iodide. By the use of the ill-defined long-wave limit of continuous absorption, the latent heat of vaporization of lithium was computed to be 29.6 kcal. per g. atom (using the mean value from data on all the lithium halides). On the assumption that the second absorption region corresponds to dissociation into a normal metal and an excited halogen atom, the excitation potentials of bromine and iodine were computed from the frequency difference between the two absorption limits on the long-wave side, giving for bromine 0.46 volt and for iodine 0.91 volt.

FIGURE 109.

Potential Energy Curves for a Heteropolar Molecule (Rabinowitsch, *Z. Electrochemie*).

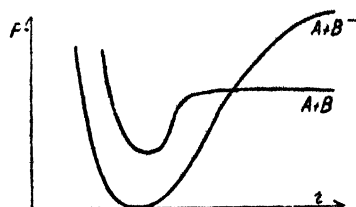


Figure 109 illustrates the potential energy curves which characterize a heteropolar molecule. The crossing of the curves is necessary because the energy of a system of two ions must be greater than that of the same two atoms, however excited. The crossing is a point at which the potential energy is the same for a given atomic separation for both the excited and ground states. A molecule at this point may dissociate in either manner so that the molecule cannot be either exclusively homopolar or heteropolar. In some cases the probability of the dissociation following one course exceeds that of its following the other. This is the more likely the greater the energetic separation of the two curves.

It has thus become evident that a simple classification of molecules into heteropolar and homopolar is unnecessary and arbitrary. The view that a given molecule shares the distinguishing features of both types serves to explain the controversy regarding the nature of hydrogen chloride. This was long thought to be heteropolar because of its dissociation into ions in aqueous solutions. Kondrat'ev⁴³ advanced evidence from the convergence of its infrared bands for a homopolar nature, but Rawlins⁴⁴ believed gaseous hydrogen chloride heteropolar because of the constancy of its dielectric constant in a variable magnetic field.⁴⁵

The continuous absorption spectrum of silver iodide vapor closely resembles the spectra of the alkali chlorides.⁴⁶ It extends from 3500 to 2400Å with a maximum at 3170Å. The dissociation results in a normal silver atom and an excited iodine

⁴² Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, 2, 33 (1932); *Chem. Abs.*, 27, 2380 (1933).

⁴³ Kondrat'ev, V., *Z. Physik*, 48, 583 (1928).

⁴⁴ Rawlins, F., *Z. Physik*, 50, 440 (1928).

⁴⁵ See, however, Datta, S., and Chakroborti, B., *Current Sci.*, 3, 349 (1935).

⁴⁶ Franck, J., and Kuhn, H., *Z. Physik*, 43, 164 (1927).

atom. For dissociation into two normal atoms the absorption band would have to be of much longer wave-length. This conclusion was also confirmed by the fluorescence spectrum excited by irradiating the vapor with the copper line 3274A. The heat of dissociation calculated from the fluorescence spectrum is approximately 54 kcal., whereas that found by measuring the work of dissociation is 47 kcal. This indicates that the dissociation products are two neutral atoms and not two ions for which a heat of dissociation of 140 kcal. would be required. In the vapors of silver bromide the absorption bands lie between 3100 and 3400A and for silver chloride between 3100 and 3300A.⁴⁷ The vibration frequency changes only slightly between the initial and final electronic states, the difference decreasing from iodide to chloride. A series of resonance lines was obtained by suitable illumination of the vapors. From these the heat of dissociation of silver bromide is roughly estimated at 2.5 volts, in agreement with the thermochemical value, 2.6. This shows that in the vapor state these molecules are non-polar. The true heats of dissociation are closely related to the constants of the quasi-elastic binding forces obtained from the vibration frequency in the normal state. It is therefore concluded that the electron linkage is similar for the three silver halides. Brice⁴⁸ finds the absorption of silver bromide and iodide vapors to be continuous below 3350A, with maxima about 3170A for both. The heat of dissociation for the normal states is 2.77 volts (silver bromide) and 3.02 volts (silver iodide), and for the excited states 0.21 and 0.10 volt, respectively. It could not be determined whether the products were metastable halogen and normal silver or metastable halogen and excited silver. Dutta⁴⁹ claims the normal form of silver halides in the vapor state to be ionic and not atomic.

Herzberg⁵⁰ has summarized the spectroscopic methods for determining the dissociation energies of diatomic molecules. These methods have been extended to polyatomic molecules. Mecke,⁵¹ who discussed the mechanism of dissociation of molecules such as water, carbon dioxide, methane, formaldehyde and the nitrogen oxides, suggested that that atom is split off first which represents the smallest energy of dissociation.⁵²

Terenin⁵³ observes that the photodecomposition of SnI_4 vapor by light of 2500-2150A is accompanied by a bright visible emission of the spectrum of the iodine molecule with an abnormal distribution of intensity in the bands. The iodine molecule is thought to be detached in one primary process. The whole process is equivalent to a recombination of the atoms in the act of photodissociation, or to a redistribution of the valency linkings. A marked temperature coefficient indicates the necessity for an energy of activation for this type of photodissociation. The mechanism of the yellow fluorescence in the vapor of bismuth iodide may be similarly explained; under the action of suitable quanta and with some thermal activation an iodine molecule may be detached from BiI_3 .⁵⁴

⁴⁷ Franck, J., and Kuhn, H., *Z. Physik*, **44**, 607 (1927).

⁴⁸ Brice, B. A., *Phys. Rev.*, **38**, 658 (1931).

⁴⁹ Dutta, A. K., *Trans. Bose Research Inst. Calcutta*, **8**, 248 (1932-3); *Chem. Abs.*, **29**, 6839 (1935).

⁵⁰ Herzberg, G., *Chem. Rev.*, **20**, 145 (1937).

⁵¹ Mecke, R., *Z. physik. Chem.*, **7B**, 108 (1930).

⁵² See also Kimura, M., *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **18**, 150 (1932).

⁵³ Terenin, A., *Nature*, **135**, 543 (1935); *Compt. rend. Acad. Sci. U.R.S.S.*, **1**, 482 (1934); **3**, 181 (1935); *Brit. Chem. Abs.*, **A**, 807 (1935); Terenin, A., and Tshubarov, R., *Acta Physicochim. U.R.S.S.*, **7**, 1 (1937); *Chem. Abs.*, **32**, 3266 (1938); Parti, Y. P., and Samuel, R., *Proc. Roy. Soc.*, **49**, 568 (1937); see also Herzberg, G., and Teller, E., *Z. physik. Chem.*, **21B**, 410 (1933)] and van Manen, B., *Chem. Weekblad*, **34**, 549 (1937)] for polyatomic molecules.

⁵⁴ See also Neulmin, H., *Physik. Z. Sowjetunion*, **2**, 422 (1932). For zinc and cadmium halides, see Deb, S., *Trans. Bose Research Institute, Calcutta*, **10**, 223 (1934-5); *Chem. Abs.*, **32**, 3263 (1938).

In the Schumann region, many molecules of inorganic or simple organic compounds become fluorescent because of dissociation into radicals, some of which are excited.⁵⁵ It is, however, unnecessary to discuss in detail the many contributions of spectroscopy to the heats of dissociation of inorganic compounds. The most accurate recent values for the heats of dissociation of various compounds as obtained by all available methods have been compared and tabulated by Rossini and Bichowsky.⁵⁶ The band spectra of many compounds will be discussed briefly in the consideration of individual photochemical reactions in the remaining chapters.

PREDISSOCIATION SPECTRA

One feature of the band spectra of certain compounds requires special mention. Franck⁵⁷ as early as 1925 mentioned band spectra in which the rotational structure, sharp within the bands at longer wave-lengths, becomes diffuse at shorter ones. He gave the interpretation, no longer regarded as correct, that the rotational energy in such cases is actually great enough to dissociate the molecule. Such spectra had been described by Henri and Teves⁵⁸ who called them predissociation spectra. By 1929 this type of absorption had been observed in the spectra of more than 40 polyatomic molecules, such as sulfur dioxide, ammonia, nitrogen peroxide, etc. It is not, however, confined to polyatomic molecules, being exhibited by some diatomic molecules. Indeed, it was first discovered in the case of sulfur vapor in the bands of which the rotation lines disappear at 2792Å, although the

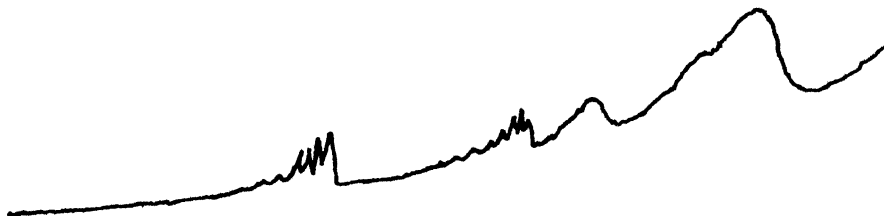


FIGURE 110. Predissociation of NO_2 . (Bonhoeffer and Harteck, "Grundlagen der Photochemie," Courtesy, Th. Steinkoff, Dresden).

vibrational bands continue to shorter wave-lengths. Figure 110, showing the absorption of nitrogen peroxide, illustrates the phenomenon. In the bands at 2491 and 2459Å, the quantized rotation lines are clearly evident, but they have disappeared in the vibration bands at 2447 and 2425Å. In some, but not all, cases the region of predissociation is followed on the short-wave side by a region of continuous absorption. In other cases, the diffuse bands are found on both the long- and short-wave sides of bands with definite rotation lines so that a molecule may exhibit more than one region of predissociation.

Henri suggested the name predissociation because he believed that absorption in this region produced a new state of the molecule in which the latter is chemically active, labile, non-fluorescing and predisposed to dissociate. More recent studies have somewhat altered this concept. The interpretation of the phenomenon by the aid of potential energy curves and by the aid of an analogy with the Auger

⁵⁵ Neuhäuser, H., and Terenin, A., *Bull. Acad. Sci. U.R.S.S., Classe sci. math. nat., Ser., phys.*, 529, 1936; *Chem. Abs.*, 31, 3790 (1937).

⁵⁶ Rossini, F. D., and Bichowsky, F. R., "Thermochemistry of Chemical Substances," New York, Reinhold Publishing Corp., 1936.

⁵⁷ Franck, J., *Z. Elektrochem.*, 31, 350 (1925).

⁵⁸ Henri, V., and Teves, M. P., *Nature*, 114, 894 (1924); *Compt. rend.*, 179, 1156 (1924).

effect in x-ray spectra⁵⁹ has been the subject of much work.⁶⁰ New criteria for the presence of this type of absorption have been given by Kaplan⁶¹ who has investigated nitrogen spectra.⁶²

In brief, it may be said that the phenomenon depends upon the existence of two excited states of the molecule the potential energy curves for which cross at a position which represents binding for one state and dissociation for the other. In Figure 111, the ground states are not represented for the molecules considered. In each case transitions from the ground state to excited state A are permitted but those to excited state C are forbidden. Assume that by the Franck-Condon principle the electron transition has raised the energy to the points marked X.⁶³ If only the state C existed, the molecule would suffer dissociation either immediately or after completing a half vibration. If, on the other hand, only the states A were possible, excited molecular states would result and these would account for the production of bands with rotational fine structure. After a brief life (10^{-8} second), they would emit part or all of their excitation energy as fluorescence. But when,

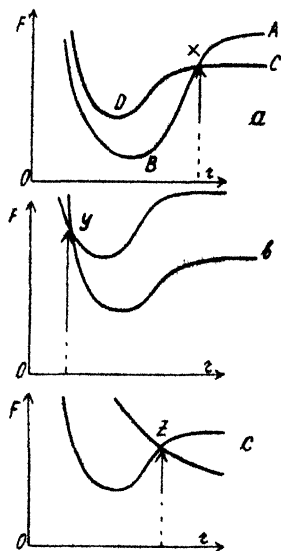


FIGURE 111.

Potential Energy Curves for Predissociation
(Rabinowitsch, *Z. Electrochemie*)

as in the figure, two crossed excited states may exist, the molecule may vibrate along either curve. Thus a molecule if excited may during its life of 10^{-8} seconds perform many vibrations the period of which is of the order of only 10^{-13} second before it emits its energy as fluorescence. While it remains as a molecule, it is also rotating and a rotational line (or lines from different ones of the many molecules) is produced within the vibrational band. But during each time that, in the course of a vibration, it passes through the crossing point, the excited molecule stands a finite chance of changing by a "radiationless transition," which involves no change in potential energy, to curve C which leads to dissociation. Thus it is

⁵⁹ Bonhoeffer, K., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1927)

⁶⁰ Herzberg, G., "Die Predissociation und verwandte Erscheinungen," Springer, Berlin (1931), *Phys. Rev.*, **40**, 313 (1932).

⁶¹ Kaplan, J., *Phys. Rev.*, **38**, 1079 (1931).

⁶² Kaplan, J., *Phys. Rev.*, **41**, 114 (1932).

⁶³ Franck, J., and Sponer, H., *Nachr. Ges. Wissen. Göttingen*, 241 (1928).

that a single electronic transition gives (in the case of some of the molecules) rotational lines within a vibrational band while other molecules suffering the same electronic excitation undergo dissociation.

The width of each line of a spectrum is dependent upon the life of the excited state. In general, the longer the life, the narrower the line.⁶⁴ The net result of the dissociation of some of the molecules is to shorten the mean life of the excited molecules; the effect of this is to broaden the rotational lines of the absorption band. Because of this tendency the vibrational bands assume the diffuseness characteristic of predissociation. A second effect is a lessening of the intensity of the fluorescence. Fluorescence measurements offer an even more sensitive criterion for predissociation than does the effect of line-broadening although this test can only be used in gases at low pressures. Otherwise the fluorescence might be greatly affected by collisions.⁶⁵

There are "selection rules" concerning the states which may exhibit predissociation,⁶⁶ but their consideration would lead us too far into specialized fields of molecular spectra. From a photochemical standpoint, in which we are primarily interested, the significance of the predissociation regions is that they represent regions of optical dissociation and as such are capable of yielding information in regard to the primary photochemical process in the reactions of the substances which exhibit such predissociation regions.

Since in the predissociation region the excitation energy must be at least equal to the dissociation energy, it is possible to calculate a maximum value for the normal heat of dissociation from the wave-length at which the diffuse spectrum commences, or the fluorescence lessens.⁶⁷ This can be done only when the horizontal portion of the dissociation curve is cut by the excited curve. As this appears to be the case in numerous instances, such calculations have often yielded heats of dissociation in agreement with those obtained by other methods. The two predissociation limits observed by Henri in nitrogen peroxide at 3700Å (NO and O) and 2459Å (NO and excited O) correspond to 72.2 and 117 kcal. The difference between these fixes the energy of excitation of oxygen at 45 kcal.⁶⁸ Similarly calculations of the heat of dissociation of oxygen have been made from the predissociation spectrum of sulfur dioxide. From predissociation limits, Bates⁶⁹ has calculated the heats of dissociation of OH and NH to be 116.05 and 102.2 kcal. Urey and Johnston⁷⁰ find the predissociation limit of chlorine dioxide to indicate an energy of dissociation through one mode of vibration of the excited electronic state into a ClO molecule and an oxygen atom.

Predissociation may be induced in certain cases in spectral regions normally showing discrete band spectra, by the addition of other gases. The change of absorption spectrum is practically independent of the nature of the foreign gas, at least in the case of the visible bromine spectrum observed by Avramenko and Kondrat'ev.⁷¹ External magnetic fields may also cause induced predissociation.⁷²

⁶⁴ The details of the theory of this relation must be sought in physical texts. The application of the Heisenberg uncertainty principle is involved. See also Rice, O. K., *Phys. Rev.*, **33**, 748 (1929); *J. Chem. Physics*, **1**, 375 (1933) and Kronig, R. de L., *Z. Physik*, **50**, 347 (1928).

⁶⁵ Kondrat'ev, V., and Polak, L., *Z. Physik*, **76**, 386 (1932).

⁶⁶ Kronig, R. de L., *Z. Physik*, **62**, 300 (1930).

⁶⁷ Turner, L. A., *Z. Physik*, **68**, 178 (1931).

⁶⁸ See also Herzberg, G., *Z. physik. Chem.*, **10B**, 189 (1930).

⁶⁹ Bates, J. R., *Z. physikal. Chem. Bodenstein Band*, 329 (1931).

⁷⁰ Urey, H. C., and Johnston, H., *Phys. Rev.*, **38**, 2131 (1931).

⁷¹ Avramenko, L., and Kondrat'ev, V., *Physik. Z. Sowj.*, **10**, 741 (1936); *Chem. Abs.*, **31**, 8366 (1937). See also Loomis and Fuller, *Phys. Rev.*, **39**, 180 (1932); Kondrat'ev, V., and Polak, L., *Physik. Z. Sowj.*, **4**, 764 (1933).

⁷² Turner, L., *Phys. Rev.*, **41**, 627 (1932).

A general discussion of induced predissociation and the predissociation of polyatomic molecules has been given by Burton and Rollefson.⁷³

The principles followed in interpreting the predissociation spectra of diatomic molecules require amplification when applied to the spectra of polyatomic molecules so as to take into account the more complex nuclear vibrations and the fact that polyatomic products of decomposition contain vibrational and rotational energy, while for monatomic dissociation products only electron excitation energy need be considered. In the case of sulfur dioxide,⁷⁴ the energy value for the predissociation limit at 1950 Å is greater than the energy required for thermal dissociation into SO and O by about 13 kcal.; this must be divided between translational and vibrational and even some rotational energy.

A marked shifting of the region of predissociation to longer wave-lengths with increase in the temperature of the absorbing gas was noted by Henri in his work on predissociation. Joos and Hermann⁷⁵ have confirmed Herzberg's suggestion that this is due to the thermal excitation of higher vibrational levels in the ground electronic state, by observations on nitrogen peroxide at temperatures from -15° to 500° . These show that the sharpness of the individual bands is not affected by the rise in temperature. The temperature effect is of some significance for the temperature coefficients of certain photochemical changes.

Caution must be used in concluding that photochemical reactions brought about by light absorbed in a region of sharply banded absorption have an excited molecule mechanism,⁷⁶ since induced predissociation may occur in molecules showing any kind of light absorption. Furthermore, weak continuous absorption between the lines of a spectrum must not be neglected. Consideration of such absorption in the chlorine spectrum at wave-lengths longer than the convergence limit has led to a recent revision of the interpretation of the mechanism of the combination of hydrogen and chlorine induced by light in this region.⁷⁷

Franck and Rabinowitsch⁷⁸ have stated that in the majority of photochemical reactions in gases every act of absorption leads to dissociation into atoms or free radicals, a point of view in which Lowry⁷⁹ concurs. West⁸⁰ tests for the paramagnetic free radicals by ability of the latter to effect the ortho-para hydrogen conversion. He applied the method with success to the detection of methyl radicals produced by the irradiation of methyl iodide and of acetone vapors. However, benzene and propionaldehyde when illuminated did not cause the ortho-para hydrogen conversion. Neuimin⁸¹ uses a layer of molybdenum trioxide in the detection of atomic hydrogen, which forms an intense blue color, "molybdenum indigo."

⁷³ Burton, M., and Rollefson, G. K., *J. Chem. Phys.*, **6**, 416 (1938). For the case of sulfur, see Olsson, E., *Naturwiss.*, **25**, 781 (1937) and Lochte-Holtgreven, W., *Z. Physik*, **109**, 147, 149 (1938).

⁷⁴ Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932). For a general theoretical discussion of the predissociation of polyatomic molecules, see Dushinskii, F., *Acta Physicochim. U.R.S.S.*, **5**, 651 (1936).

⁷⁵ Joos, G., and Hermann, A., *Physik. Z.*, **33**, 213 (1932).

⁷⁶ Rollefson, G. K., *J. Phys. Chem.*, **42**, 737 (1938).

⁷⁷ Bayliss, N. S., *Trans. Faraday Soc.*, **33**, 1339 (1937).

⁷⁸ Franck, J., and Rabinowitsch, E., *Trans. Faraday Soc.*, **30**, 120 (1934).

⁷⁹ Lowry, T. M., *Trans. Faraday Soc.*, **30**, 3 (1934).

⁸⁰ West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935).

⁸¹ Neuimin, H., *Compt. rend. acad. sci., U.R.S.S.*, **16**, 447 (1937); *Chem. Abs.*, **32**, 1580 (1938).

Chapter 15

Overall Photochemical Reactions

It has been shown in the preceding chapters that it is advantageous to consider separately the mechanisms of the primary and secondary processes of photochemical reactions. Experimentally, however, there is no such demarcation and both must be studied simultaneously.

It is now generally recognized that for chemical reactions to proceed the molecules must be supplied with at least a minimal amount of energy known as the activation energy. This is usually not identical with the observed heat of reaction, the latter being merely the difference between the activation energies for the forward and reverse reactions. In purely thermal reactions, the activation energy is kinetic energy due to random collisions resulting from the heat motion of the molecules. Only those molecules which at the experimental temperature have energies in excess of the activation energy are capable of reacting. Since from the Maxwell-Boltzmann distribution law at ordinary temperatures only about one in 10^7 molecules of a gas possesses an energy equivalent to 25 kcal. per mole, reactions for which the activation energy is greater than this will be slow. The absorption of ultraviolet light may, however, readily supply the molecules with far greater amounts of energy so that the photochemical reaction may be rapid. Thus, the processes of dissociation or excitation attendant upon the absorption of light may yield atoms, free radicals or molecules with sufficient activation energy to allow the remaining secondary reactions to proceed readily.

Whether or not the secondary reactions do so depends upon the nature of the secondary reactions in which these primary products participate. If all the secondary reactions proceed at the experimental temperatures with negligible activation energies, or with activation energies compatible with those possessed by the primary products, the photochemical reaction will proceed. The rate of reaction is then determined by that of the primary process, which depends upon the rate of absorption of energy. If, on the other hand, the secondary processes require activation energies in excess of those possessed by the primary products the reaction will not proceed. In such cases, the temperature must be raised to one at which the requisite activation energy for the slowest necessary secondary process is available. The overall reaction will then have a temperature coefficient. In general, the primary process is not markedly dependent upon temperature, and purely photochemical reactions have temperature coefficients of unity. This means merely that none of the secondary processes requires activation energy. When there is a temperature coefficient, it is usually due, therefore, to one of the secondary processes requiring activation energy not sufficiently available at the usual experimental temperatures. Since most photoreactions occur through the intermediate formation of atoms and free radicals, an accurate knowledge of the rate constants of reactions in which these participate is of importance for the determination of the mechanisms of individual photoreactions.¹

¹ Bates, J. R., *Chem. Rev.*, **17**, 401 (1935).

PHOTOCHEMICAL THRESHOLDS

Since it is the function of light in a photochemical reaction to supply the energy of activation for that reaction (or more strictly for its primary process), it should be necessary to employ a radiation of frequency corresponding to at least that energy. This implies the existence of a photochemical threshold frequency below which the reaction could not be brought about. Mecke² states that the accurate determination of this threshold wave-length is important for a proper understanding of the nature of the primary process, but notes that it unfortunately presents great experimental difficulties. Indeed, some workers have indicated these difficulties to be so great as to preclude experimental determination.

In the case of the combination of hydrogen and chlorine, Coehn and Jung³ claimed to have found a threshold at 5400A, longer wave-lengths not leading to the formation of hydrogen chloride. On the other hand, Taylor⁴ placed the threshold at 4900A. Both of these results were criticized by Bowen,⁵ who showed that the results indicated no more than that the rate of reaction is proportional to the amount of light absorbed and that this drops to low values in these wave-length regions.

A similar attempt to find critical wave-lengths for the decomposition of ethyl and methyl iodides was due to Job and Emschwiller.⁶ They considered the quantum at the critical wave-length for the decomposition (the "critical complement"), to measure the binding energy of the covalence C-I. By placing a tube of ethyl iodide in the spectrum of a carbon arc, it was noted that the reaction appeared to proceed as soon as wave-lengths shorter than 4100A were used. This corresponds (Figure 103) to 69.3 kcal. per mole. Methyl iodide gave this same value, but for iodobenzene it was 4000A or 71 kcal. However, Bowen⁷ criticized these conclusions by showing that the threshold values were related either to the lower limits of the absorption spectrum or to the wave-length of maximum absorption. Bowen stated there was no theoretical justification for such conclusions. Warburg had attempted to relate thresholds to the heat of linking. The thermal values for the C-I linking gave only 40 kcal., whereas Job and Emschwiller had found 69.3 kcal. As has been indicated in an earlier chapter the heat of dissociation of such molecules as iodine into normal atoms is not related to the actual amounts of energy required to dissociate the molecule into a normal and an excited atom; this may be far greater. Therefore, heats of linking could not be calculated even from a knowledge of the convergence limit without a knowledge of the amount of excitation energy of the decomposition products. Allmand and Reeve⁸ found the decomposition of oxalic and formic acids to proceed at a measurable rate in light of wave-lengths much longer than those computed by Volmar⁹ from thermochemical data on the heats of unimolecular decomposition.

Schneider and Sperti¹⁰ suggested the existence of threshold wave-lengths for

² Mecke, R., *Trans. Faraday Soc.*, **27**, 360 (1931).

³ Coehn, A., and Jung, G., *Z. physik. Chem.*, **110**, 705 (1924).

⁴ Taylor, W., *Phil. Mag.*, **49**, 1165 (1925).

⁵ Bowen, E. J., *Phil. Mag.*, **50**, 879 (1925).

⁶ Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52, 168 (1924).

⁷ Bowen, E. J., *Trans. Faraday Soc.*, **21**, 543 (1926).

⁸ Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, **129**, 2852 (1926).

⁹ Volmar, *Compt. rend.*, **178**, 697 (1924); **180**, 1172 (1925).

¹⁰ Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 7 (1926).

photochemical reactions. By means of a series of filters they found the longest wave-length capable of liberating iodine from a solution of potassium iodide to lie between 3340 and 3660Å. Inasmuch as wave-bands covering as much as 320Å units had to be used, it was not possible to determine whether or not the yield dropped suddenly to zero from fairly high values over a very narrow range of wave-lengths. These authors extended their point of view to the inactivation of the enzymes pepsin, rennet and invertase and to the killing of bacteria and protozoa as well.

Further tests of the question require accurate determinations of the quantum yields at a series of wave-lengths; a positive threshold would be indicated by a sudden drop to zero from a fairly high and constant quantum yield. Comparatively few such data are available, but those papers in which data adequate to the test have been given, *e.g.*, the work of Norrish¹¹ on the decomposition of nitrogen dioxide, indicate a sloping curve over a fairly wide range of wave-lengths. For this reaction the quantum yield is zero at 4360Å, 0.72-0.74 at 4050Å, 1.54-2.10 at 3650Å and 2.07 at 3100-2700Å. A possible explanation of the lack of sharpness in the change in quantum yield with wave-length may be that not all of the molecules of the absorbing material are initially in the same vibrational state. Those few molecules which at the temperature of the experiment may be in excited states may be expected to be activated by the absorption of smaller quanta than are required to activate those initially in lower vibrational states.¹² The heat of dissociation obtained spectroscopically by the absorption of a gas at a temperature other than absolute zero is the weighted mean of the heats of dissociation of the various vibrational excited states existing at the temperature at which the absorption occurs. Conversely, since these states have different heats of dissociation, the wave-length threshold for each should be definite, but for the mixture there should only be a sloping curve or a diffuse threshold.

By extrapolating the quantum yields of each of four reactions to a zero quantum yield, Rao and Dhar¹³ found extrapolated threshold wave-lengths. The corresponding energies in kcal. per mole were found to agree closely with the energy of activation of the dark reactions. There was, however, in some of these a rather extended and uncertain extrapolation. Bowen had found much earlier that the activation energies of four bimolecular reactions calculated from their temperature coefficients could not be related to the energies corresponding to the long-wave limits of the absorption bands. Neither the absorption limit nor the activation energy bore any definite relation to the heats of linking of the bonds assumed to be ruptured in the photochemical processes.

Franck and Herzfeld¹⁴ have emphasized the possibility, at least for polyatomic molecules, that thermal energy can contribute much more of the energy required for a photochemical change than had previously been assumed. Also, in such complicated molecules more than one absorbing center may be present. Energy absorbed by one linking may be transferred to another, which itself absorbs, so that the sum or a portion of the sum of the energies absorbed in separate portions of the molecule may be made available to affect a disruption of one or the other linking, the energy absorbed by that linking alone being insufficient for this purpose. The possibility of such intramolecular migrations of energy seems to

¹¹ Norrish, R. G. W., *J. Chem. Soc.*, 1604 (1929).

¹² Tolman, R. C., *J. Am. Chem. Soc.*, 42, 2506 (1920); 45, 2285 (1923).

¹³ Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, 36, 646 (1932).

¹⁴ Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, 41, 97 (1937).

have been definitely shown in the work of Norrish on the photochemistry of the aldehydes. (Chapter 22.)

Over wide ranges of wave-lengths there may be variations in the quantum yield with the wave-length. In many reactions, the quantum yield increases with the frequency. In the case of the hydrolysis of tetrachloroplatinic acid¹⁵ the yield continues to increase over a range of 3080Å, which corresponds to a range of energy levels far too great to be accounted for on the basis of a temperature distribution of vibrational states. The reasons for this phenomenon are not yet clear. Such results appear to be obtained chiefly in reactions involving polyatomic molecules in solution.

TEMPERATURE COEFFICIENTS

Since the secondary processes are thermal reactions, they may be expected to possess temperature coefficients different from unity. Nevertheless, early observations by Eder (1879) and by Goldberg¹⁶ indicated most of the then known photochemical reactions to have temperature coefficients close to unity. Bancroft and Allen¹⁷ disagreed and several reactions with higher values were brought forward by Plotnikow,¹⁸ who proposed to classify photochemical reactions into three groups with temperature coefficients of 1.04, 1.20 and 1.45, respectively. Most reactions were thought to belong to the first group. The second group contained a few reactions in which it was suggested that diffusion processes determined the rate.¹⁹ The third group comprised chiefly those reactions in which halogens were the absorbers. In determining the temperature coefficient, the effects of a possible dark reaction had to be eliminated either by working at very low temperatures and with light of high intensity or by subtracting dark rates determined in separate experiments. This latter step assumed the principle of the additivity of the rates of light and dark reactions, a principle for which there is little present justification.

The data at present available for a large number of reactions²⁰ show the distribution of temperature coefficients to be random, so that the Plotnikow classification into three groups has lost significance. Furthermore, the idea that the halogens fall into a special class was disproved by Hertel,²¹ who found that the temperature coefficient for the hydrogen-chlorine combination has different values when light of different wave-length regions is employed. With light in the region of the band spectrum of chlorine, the temperature coefficient is 1.48, but with light within the continuous region at shorter wave-lengths, it is 1.37. In the presence of traces of oxygen, the true values may be masked, since 1.12 was stated to be the temperature coefficient of the reaction under such conditions.

It was early recognized that the temperature coefficient for a dark reaction should be expected to be higher than for a light reaction.²² An indication of the

¹⁵ Cited by Style, D. W. G., "Photochemistry," p. 69, Methuen, 1930, from Boll, M., *Ann. Physique*, **25**, 243 (1914).

¹⁶ Goldberg, E., *Z. physik. Chem.*, **41**, 1 (1903); *Z. wiss. Phot.*, **4**, 56 (1906).

¹⁷ Bancroft, W. D., and Allen, R. P., *Proc. Nat. Acad. Sci.*, **15**, 445 (1929).

¹⁸ Plotnikow, J., *Z. physik. Chem.*, **78**, 573 (1911).

¹⁹ See for certain reactions in liquid systems, Berthoud, A., and Bellenot, H., *J. chim. Phys.*, **21**, 308 (1924). Abel, E., and Schmid, H., *Monatsh.*, **61**, 361 (1932), find the temperature coefficient of a streaming reaction smaller than that of a quiet one.

²⁰ For tabulations of temperature coefficients, see Plotnikow, J., "Allgemeine Photochemie," 2nd Ed., de Gruyter, Berlin, 1936. Kistiakowsky, G. B., "Photochemical Processes," New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1928.

²¹ Hertel, E., *Z. physik. Chem.*, **15B**, 325 (1932).

²² Bodenstein, M., *Z. physik. Chem.*, **85**, 380 (1913).

²³ Banerji, R. C., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **134**, 172 (1924); *Chem. Abs.*, **18**, 2634 (1924).

relative magnitudes of the light and dark temperature coefficients for a number of reactions was given by Banerji and Dhar.²⁵ The decomposition of trichloroacetic acid has a temperature coefficient of 3.0 in the light and of 4.28 in the dark. For the inversion of cane sugar they give the values 3.4 and 3.82, for the oxidation of sodium nitrite by iodine, 1.4 and 2.5, and for the action between oxalic and hydriodic acids 2.2-2.5 and 2.98 respectively.

Indian workers have devoted considerable attention to such determinations.²⁴ In general, it has been found that the temperature coefficients of light reactions vary with the wave-length of the incident light, although the coefficients are usually less than those of the corresponding thermal reactions. The greater the extent to which a reaction is accelerated by light, the smaller is the value of the temperature coefficient. Yajnik and Uppal were unable to find any relation between the temperature coefficients and the dielectric constants of the solvents employed.

Temperature coefficients less than unity are very rarely encountered. They could be interpreted as meaning that the temperature coefficient of some dark inhibiting reaction in a chain mechanism is greater than that of the chain-lengthening processes.

The temperature coefficients discussed in the preceding paragraphs are those of the velocities of reactions, the light intensity being held constant. The results recounted have held little general significance. More important theoretically are the results obtained when the amount of absorbed energy is maintained constant and the coefficients are computed for the quantum yields. Such values will differ from those of velocity measurements at constant incident intensity when the measurements are not made under conditions of total absorption if there is a dependence of the extinction coefficient upon the temperature.

In some cases a complex formed in a solution absorbs some of the light, as for example, the triiodide ion in reactions involving oxidation by iodine. In such a case, the light is partly absorbed by iodine and partly by the triiodide ion, only the former being effective. The amount of triiodide ion present depends upon the temperature since the reaction for its formation has a temperature coefficient. Accordingly, the photochemical reaction will have a temperature coefficient for its quantum yield dependent upon a temperature coefficient of the efficient absorption. Such reasoning may conceivably apply also to cases in which solvation of the absorbing molecule plays a prominent part.

But there is a more fundamental sense in which the process of absorption may be attended by temperature effects—there may be a variation of the extinction coefficient of a substance with temperature. Tolman²⁵ noted the possibility that a molecule might have to be raised to an energy state higher than that of the normal state before it would be capable of absorbing certain radiations. Otherwise stated, the probability of absorption might depend upon the original quantum state of the molecule. There is evidence that the absorption coefficients of gases possess temperature coefficients. v. Wartenberg²⁶ concluded that the absorption of longer wave-lengths by oxygen at 1800°C. gave evidence of being largely due to molecules possessing a considerable amount of internal energy.²⁷ However,

²⁴ Mukerji, B., and Dhar, N. R., *J. Phys. Chem.*, **33**, 850 (1929); Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Chem. Abs.*, **24**, 1035 (1930).

²⁵ Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).

²⁶ v. Wartenberg, H., *Physik. Z.*, **11**, 1168 (1910).

²⁷ See also observations on bromine by Ribaud, G., *Ann. Physique*, **12**, 107 (1919), and on chlorine by Dobbie, J. J., and Fox, J. J., *Proc. Roy. Soc.*, **99A**, 456 (1921) and by Kubn, H., *Z. Physik*, **39**, 77 (1926).

the effects of temperature on light absorption are generally insufficient to account for the temperature coefficients of photochemical overall reactions. Since electronically excited states cannot be excited by thermal means, at least within the temperature ranges usually under consideration, the possibility of getting excited states is limited to that of vibrational states. However, for most gases, the number of molecules in any but the lowest few vibrational levels can usually be neglected. For this reason, the possibility raised by Tolman apparently is not of great practical significance. Young and Style²⁸ have given a detailed discussion of the manner in which a study of the temperature coefficient of a reaction may give information as to its mechanism. According to Dhar and Bhattacharya,²⁹ an increase in the absorption of light by a molecule is associated with increased chemical reactivity and a weakening of the binding forces. When a molecule becomes more reactive because of an increase in temperature or the presence of sensitizers it is likely to absorb light more markedly. It has been reported by Dhar and Bhargava,³⁰ that in certain cases, the light absorption of a mixture of substances may be greater than the sum of the absorptions of the separate substances. The increased absorption is attributed to an activation of molecules by the presence of other molecules. Fast reactions are claimed to show greater light absorption than do slower ones.

It is possible to eliminate the question of temperature effects on absorption when variations in the temperature coefficients do not occur in systems having a wide range of variation of the original concentration of the absorbing component. When effects due to a variation of the primary process with temperature can be eliminated, as is most generally the case, the temperature coefficients of the quantum yields of photochemical reactions give information regarding the mechanism of the secondary processes.³¹ As such, they can best be discussed in connection with the individual reactions in which they are encountered. In general, it has been recognized that the temperature coefficients decrease as shorter wave-lengths of light are employed.³² The use of shorter wave-length light usually gives an increased quantum yield but a smaller temperature coefficient, but exceptions are known.

Most of the sources of a temperature effect of a quantum yield—diffusion, change in viscosity of a solvent, thermal activation of some one of the secondary reactions—would tend to produce definite values of some energy of activation at the temperature of measurements, or else would cause the calculated thermal activation energy for an intermediary process to decrease when determined at higher temperatures. Nevertheless, Kistiakowsky³³ has found in two reactions—the oxidation of hydrogen and that of carbon monoxide, irradiated by an aluminum spark—temperature coefficients which increased with temperature. Style³⁴ makes the suggestion that in such cases collisions of the products of some highly exothermic secondary reaction with the absorbing molecules may activate the latter, some thermal activation energy being required for this process.

²⁸ Young, K. W., and Style, D. W. G., *Trans. Faraday Soc.*, **27**, 493 (1931).

²⁹ Dhar, N. R., and Bhattacharya, A. K., *Z. anorg. Chem.*, **176**, 372 (1928); *J. Indian Chem. Soc.*, **11**, 33, 311 (1934); *Chem. Abs.*, **28**, 3663, 6636 (1934).

³⁰ Dhar, N. R., and Bhargava, P. N., *Nature*, **134**, 848 (1934).

³¹ Young, K. W., and Style, D. W. G., *loc. cit.*

³² Padoa, M., *Atti accad. Lincei*, **25** (II), 168, 215 (1916); **24** (II), 97, 828 (1915); *Gazz. chim. ital.*, **55**, 87 (1925).

³³ Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

³⁴ Style, D. W. G., "Photochemistry," Methuen, 75, 1930.

KINETICS OF PHOTOCHEMICAL REACTIONS

Many attempts to generalize regarding the rates of photochemical reactions have been made, but these have not proved very profitable because of the great complexity of the individual processes encountered. Conditions affecting the rate of absorption of light introduce many variables not encountered in the study of the kinetics of thermal reactions. The speed of stirring may influence the rate when most of the light is absorbed close to the window through which it enters. Photochemical processes may be aided by, opposed by, or independent of simultaneous thermal processes. The order of a given reaction conducted thermally may differ from that when it is conducted photochemically.

Bodenstein³⁵ believed the rate of absorption of light to be the principal factor controlling the velocity of photochemical reactions. The concentration of molecules other than the ones which absorb radiation was also recognized as an important factor. The simple law relating the rate of the reaction to the absorbed energy $dx/dt = KI_{\text{abs}}$ is applicable only when the possibility of the transfer of the absorbed energy to other molecules by collisions is negligible.³⁶

Wegscheider³⁷ developed a series of kinetic expressions based upon the conception that the rate is proportional to the light absorbed in a localized volume of the reaction mixture, rather than to the amount absorbed within the total volume. He extended his mathematical treatment³⁸ to the velocities of reactions with intermediary formation of excited molecules. Wegscheider believed the intensity of the light to enter the equation for the rate of formation of a product not as the first power, but as a power which gradually decreases to zero as the intensity decreases. The total absorption from the start of the reaction to the exhaustion of the absorbing component might, however, be independent of the intensity. He emphasized the possibility that the quantum yield might vary considerably during the course of a reaction, so that values determined over only a selected time interval might be more or less fortuitous. He noted also that only in cases in which the fate of the excited molecule follows a unimolecular law and the primary process is irreversible should it be expected that the quantum yield would be one. Recently, Wegscheider³⁹ has treated several systems by taking into account the light absorbed by the solvent and the reaction products as well as by the reacting substances. It is obvious that the secondary processes may be so complex in the individual case and so varied from reaction to reaction that attempts at generalizations in regard to the kinetics of overall reactions are not likely to be successful.

Several workers have attempted to classify reactions into those which are proportional to the first power of the light intensity and into those proportional to the square root of the intensity. From studies of nine inorganic reactions, Bhattacharya and Dhar⁴⁰ found two (those between chromic and oxalic acids and between potassium persulfate and potassium iodide) in accord with the first power law. The others were proportional to the square root of the intensity. They believed the latter to be the case for reactions with atomic oxygen as an inter-

³⁵ Bodenstein, M., *Trans. Faraday Soc.*, 21, 525 (1926).

³⁶ For the dependence of the velocity of a photochemical reaction on the intensity of illumination, see also Gaviola, E., *Anales assoc. quim. Argentina*, 18, 133 (1930).

³⁷ Wegscheider, R., *Rec. trav. chim.*, 44, 1118 (1925); *Z. physik. Chem.*, 103, 273 (1922).

³⁸ Wegscheider, R., *Monatsh.*, 51, 285 (1929).

³⁹ Wegscheider, R., *Monatsh.*, 62, 101 (1933).

⁴⁰ Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, 175, 357 (1928); *J. Indian Chem. Soc.*, 6, 473 (1929).

mediate. They stated that if the reactants exhibit marked absorption of light, the velocity of the reaction increases in proportion to, or more rapidly than in direct proportion to, an increase in the intensity of the light. For systems with but slight absorption of light, they considered the square root law to be valid. It was found possible in many cases to alter the rate of the dark reaction by the addition of accelerators or inhibitors. By increasing the dark rate and exposing the system to radiation which could be only slightly absorbed, a true photochemical reaction proportional to the square root of the intensity of the incident radiation or to the amount of energy absorbed, could be made to become proportional to the first power of the intensity. On the other hand, a reaction proportional to the incident intensity or to its square could be made proportional to the square root of the intensity by decreasing the velocity of the dark reaction and so increasing the photochemical velocity. These observations were extended by Mukerji and Dhar to include⁴¹ some fifteen pairs of substances. In a few reactions (sodium formate and iodine, Rochelle salt and bromine, the oxidation of quinine sulfate by chromic acid) the rate was proportional to the square of the intensity. No relation was found between the velocity of reaction of oxalic acid with potassium permanganate and the intensity of the incident light. The other reactions studied fell into the two classes described by Bhattacharya and Dhar, who believe all true photochemical reactions (with negligible dark reactions) tend to be proportional to the half or lower power of the intensity of the incident radiation.

Cases in which the rate appears to increase more rapidly than the intensity of the light are attributed by Bhagwat⁴² to the presence of inhibitors which are relatively less effective in retarding the reaction when the intensity of the light is high. Bhagwat and Dhar⁴³ also assert that when the reaction velocity is not directly proportional to the light absorption, stirring will tend to increase the rate and decrease the temperature coefficient. However, when the velocity is directly proportional to the absorption, stirring will have no effect on the velocity of the reaction or the temperature coefficient.

Allmand⁴⁴ found that if the product of the extinction coefficient and the thickness of the absorbing layer is very small, the quantum efficiency for any wavelength is inversely proportional to the square root of the rate of energy absorption. If the thickness of the absorbing layer is continuously increased from a very small value until it becomes great enough to make the absorption of the incident energy complete, the limiting value of the quantum efficiency is twice as great as that in thin layers.

Recent work on chain reactions has indicated that in general the square root relation may be expected if the substance which acts as intermediary in carrying the chain is formed at a rate proportional to the intensity, but does not hold when the intermediary substance is formed at a rate proportional to the square of its concentration.⁴⁵ Since in many reactions the chains are carried by atoms liberated in the primary process and since these atoms are removed by three-body collisions involving two atoms, the first-mentioned conditions are frequently met. This accounts for the number of reactions for which the square root law has been found to hold with a fair degree of approximation. Bhagwat⁴⁶ believes the square

⁴¹ Mukerji, B. K., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1308 (1928).

⁴² Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

⁴³ Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **9**, 335 (1932); *Chem. Abs.*, **27**, 27 (1933).

⁴⁴ Allmand, A. J., *J. Chem. Soc.*, 1557 (1929).

⁴⁵ Style, D. W. G., "Photochemistry," p. 51, Methuen, London, 1930.

⁴⁶ Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

root relationship is more likely to be observed in the region of high frequencies than in that of lower ones.

Attempts to relate the rates of photochemical reactions to the dielectric constants of the solvents employed have not proved very profitable. Winther⁴⁷ found that, in the photooxidation of iodoform and the polymerization of anthracene in a series of solvents, the velocity in general decreased with increasing dielectric constant of the solvent, but this could not be confirmed by Yajnik and Uppal.⁴⁸

The earlier investigations are replete with instances of photochemical induction periods, or lags between the beginning of irradiation and start of reaction, and also of after-effects or a continuation of reaction after the close of the irradiation period. These effects are no longer regarded as of great general significance, the many known examples being considered merely as features of the mechanisms of the specific reactions in which they are encountered. At present, induction periods are usually regarded as the times required for the photochemical destruction of certain inhibitors present in small quantities.⁴⁹ Reactions claimed to exhibit after-effects have been reported by Mukerji and Dhar.⁵⁰ It must be noted that in chain reactions the reaction does not cease instantly when the illumination is cut off, as the secondary reactions continue for some time until all chains are broken. Similarly, when the intermediary in the chains is being formed and a stationary concentration (at which formation and destruction of the intermediary are equal) is being built up, the rate of the overall reaction (which depends upon the rate of destruction) need not attain its full value.

The influence of surface catalysts is of importance chiefly as they influence the recombination rate of free atoms or radicals. Coehn and Heymer⁵¹ devised experiments in which hydrogen and chlorine were exposed to light without an opportunity of coming into contact with a solid surface. The formation of hydrogen chloride under these conditions proves that the reaction does not depend on an initial catalysis at a glass wall. Chapman and Grigg⁵² have found the rate of this reaction to be less in capillary tubes than in wider ones. This is interpreted as meaning that the reaction is carried out (see Chapter 18) by means of an unstable catalyst (hydrogen and chlorine atoms) the latter being formed by light; these atoms are destroyed by recombination when they come in contact with glass.

Although irradiation of a graphite catalyst almost triples the rate at which it decomposes hydrogen peroxide, the effect is smaller for irradiated lead peroxide and still smaller or even non-existent in the case of smooth or slightly platinized platinum.⁵³ In the case of the decomposition at the surface of colloidal platinum,

⁴⁷ Winther, C., *Trans. Faraday Soc.*, **21**, 595 (1926); see also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, **2**, 243 (1927).

⁴⁸ Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem. Abs.*, **A**, 174 (1930); *Chem. Abs.*, **24**, 1035 (1930).

⁴⁹ Earlier points of view are given by Purkayastha, R. M., *J. Indian Chem. Soc.*, **5**, 721 (1928); *Chem. Abs.*, **23**, 2105 (1929).

⁵⁰ Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **2**, 277 (1925); **5**, 203 (1928); *Chem. Abs.*, **23**, 41 (1929); *Quart. J. Indian Chem. Soc.*, **2**, 277 (1925); *Chem. Abs.*, **20**, 1953 (1926).

⁵¹ Coehn, A., and Heymer, G., *Ber.*, **59B**, 1794 (1926).

⁵² Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

⁵³ Pisarzhevskii, L. V., Korabel'nik, R. K., and Ruinskaya, E. S., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat.*, 931 (1934); *Chem. Abs.*, **29**, 2433 (1935).

the velocity constant is the sum of those of the action of ultraviolet light and of the colloid separately on hydrogen peroxide.⁵⁴

PHOTOCHEMICAL EFFECTS OF INTERMITTENT AND POLYCHROMATIC LIGHT

The possibility of producing different effects by irradiating a system with a given quantity of intermittent or continuous light has been studied, notably by Padoa and Vita.⁵⁵ In some reactions, they claimed to secure greater reaction velocities by the use of intermittent light. The light was obtained by employing rotating sectors with a continuous source. In some instances the yield at first increased with the number of alternations of the sectors and then decreased to a constant value.⁵⁶

Alternations of two or more colors with no periods of darkness caused a greater dependence of the yield on the velocity of alternation. Pulsating monochromatic light was also employed in some of their work.⁵⁷ The augmentation in yield depended both upon the wave-length of the light and the frequency of interruption, the maximum interruption being 560 times per second. In the oxidation of ferrous iodide by the 4607Å line, the velocity was doubled by the use of intermittent light. This maximum rate was said to occur periodically as the frequency of interruption was increased, the maxima appearing irregularly at interruption frequencies of 32, 98, 138, 157, 202, 253, 270, 318, 357, 390, 450 and 513 per second. With green light, the yield ratio was lower (1.70), and the maxima fewer in number, occurring at 22, 259 and 532 interruptions per second. With yellow light the maximum ratio was 1.62 at 311 interruptions per second. Except at frequencies between 20, 40 and 260-370 interruptions per second, the yield was unaltered by intermittent illumination with this light. Red light gave a maximum yield ratio of 1.37 at 472 interruptions per second. The authors suggested that the periodic maxima might be due to the formation of active molecules which are the seats of adiabatic transformations, and that the life of these molecules is greater the greater their energy levels. Berthoud⁵⁸ was unable to confirm the existence of these maxima.

Berthoud and Bellenot⁵⁹ and Briers, Chapman and Walters⁶⁰ have used the rotating sector method in studying reactions whose rates are proportional to the square root of the light intensity, *e.g.*, the oxidation of potassium oxalate by iodine. The rate of the reaction varies as the concentration (in a steady state) of an intermediary, here assumed to be iodine atoms. The latter were formed at a rate proportional to the intensity of the light and destroyed at a rate proportional to the square of the concentration of the intermediary. The concentration of the catalyst in the steady state can therefore be shown to be proportional to the square root of the light intensity. When the sector rotates so rapidly that the secondary processes continue throughout the interval of darkness the rate is independent of the speed of rotation. When it rotates so slowly that the intermediary is exhausted by the secondary processes during each period of darkness, or is materially lowered in

⁵⁴ Suirkin, Y., and Godnev, I. N., *J. Phys. Chem. (U.S.S.R.)*, **5**, 32 (1934); *Chem. Abs.*, **28**, 4971 (1934). For other reactions in which surface effects have been held to play a part, see Kondrat'ev, V., *Z. Physik*, **48**, 310 (1928) and Kautsky, H., de Bruijn, H., Neuwirth, R., and Baumeister, W., *Ber.*, **66B**, 1588 (1933).

⁵⁵ Padoa, M., and Vita, N., *Gas. chim. Ital.*, **57**, 187 (1927).

⁵⁶ Padoa, M., and Vita, N., *Atti II Congr. Naz. Chim. Pura Applic.*, 1256 (1926).

⁵⁷ Padoa, M., and Vita, N., *Gas. chim. Ital.*, **58**, 461 (1928).

⁵⁸ Berthoud, A., *J. chim. phys.*, **26**, 444 (1929).

⁵⁹ Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 307 (1924).

⁶⁰ Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, 562 (1926).

⁶¹ Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).

concentration during this period, the rate of the overall reaction will be lowered. By this method the life of the catalyst or intermediary has been calculated to be 0.03 to 0.12 second. Similar effects were observed by Briers and Chapman⁶¹ in the case of the photosynthesis of hydrogen bromide, the mean life of the intermediary being 0.063 second.

Since truly monochromatic radiations are idealizations, all actual photochemical reactions are produced by the simultaneous action of more than one wave-length, even though these be but slightly different. Considerable work has been expended upon the effects produced by the simultaneous use of relatively widely separated wave-lengths. Plotnikow⁶² claimed that the rate of bromination of cinnamic acid in carbon tetrachloride solution when simultaneously illuminated by several wave-lengths was less, in the ratio of 100 to 158, than the sum of the rates of the individual reactions when the wave-lengths were employed separately. Padoa and Vita⁶³ reported a confirmation of this behavior; they claimed also that the reaction rate does not decrease as the source is removed to greater distances to the extent demanded by the inverse square law. They reported a similar effect of complex light in diminishing the reaction rate of the decomposition of hydriodic acid, using 5460 and 5790 Å.⁶⁴ The opposite effect was reported in the case of the hydrogen-chlorine combination and in the action of light on direct-printing photographic paper, although in the latter case the order of the application of the wave-lengths used appeared to be a deciding factor.⁶⁵ Similar effects were also reported for the decomposition of ferric oxalate.

On the other hand, Berthoud,⁶⁶ who studied the oxidation of potassium nitrite by iodine in aqueous solution in yellow and blue light separately and together, found the effects to be purely additive. Winther⁶⁷ stated that the Italian workers neglected the induction periods of the reactions studied, employed incorrect methods of determining the rate of liberation of iodine in the hydrogen iodide decomposition, and employed erroneous transmission values for the filters.⁶⁸ It would appear that an interpretation of the Padoa experiments, assuming them to be correct, would imply that certain wave-lengths retard the effects produced by others. This raises the question as to whether any instances are known in which thermal reactions are retarded by light. Claims that such is the case were made by Chastaing⁶⁹ and by Trautz.⁷⁰ Details need not be given since re-examination of these reactions by Allmand and Maddison⁷¹ failed to confirm the existence of the retarding effect; this has since been admitted by Trautz. With Haas, however, Trautz has recently⁷² claimed that blue light accelerates and infrared retards the oxidation of benzaldehyde. It may be noted that it has frequently been suggested that the biological effects of ultraviolet rays may be annulled, at least in part by infrared rays.⁷³ However, others have proposed that the two forms of

⁶² Plotnikow, J., *Z. physik. Chem.* **79**, 641 (1912).

⁶³ Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **56**, 375 (1926); *Trans. Faraday Soc.*, **21**, 573 (1926).

⁶⁴ See also *Z. wiss. Phot.*, **28**, 153 (1930); Vita, N., *Gazz. chim. Ital.*, **63**, 223 (1933).

⁶⁵ Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **56**, 164 (1926); *Chem. Abs.*, **20**, 2951 (1926); *Gaz. chim. ital.*, **58**, 3 (1928).

⁶⁶ Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

⁶⁷ Winther, C., *Z. wiss. Phot.*, **31**, 251 (1933); **33**, 52 (1934).

⁶⁸ See also for further details of the controversy *Z. wiss. Phot.*, **32**, 185 (1933).

⁶⁹ Chastaing, P., *Ann. Chim. Phys.*, **11**, 145 (1877).

⁷⁰ Trautz, M., *Physik. Z.*, **7**, 899 (1906); *Z. Elektrochem.*, **13**, 550 (1907).

⁷¹ Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (1927).

⁷² Trautz, M., and Haas, H. E., *Z. wiss. Phot.*, **33**, 81, 129 (1934); *Chem. Abs.*, **29**, 2869 (1935).

⁷³ Pech, J. L., *J. med. Bordeaux*, **10**, 434 (1925).

radiation should be applied simultaneously.⁷⁴ The Herschel effect in photography appears to be a case in which infrared radiations annul the effects of visible or ultraviolet radiations.

Plotnikow⁷⁵ has called attention to reactions which appear to proceed at periodic rates when illumination is furnished by complex light. He believes the concentration of free halogen in solutions of either bromine or chlorine in carbon tetrachloride to undergo periodic fluctuations when irradiated for prolonged periods with complex, but not with monochromatic, light.

⁷⁴ Rowley, C. D., and Larsky, A. W., British P. 325,824 (1928).

⁷⁵ Plotnikow, J., *Z. Physik*, **32**, 942 (1925).

Chapter 16

Photosensitized Processes

In photosensitized processes, the light which causes the reaction to proceed is absorbed, not by the reactants, but by some added substance which is capable of passing on the absorbed energy, or a sufficient portion of it, to the reactants. The simplest of such processes are those in which atoms act as photosensitizers.¹ Turner reviewed the earlier work on the excited systems formed when atoms absorb definite wavelengths. Certain widely-used terms regarding the nature of collisions in which excited atoms take part were introduced by Klein and Rosseland in 1921.² They called "collisions of the first kind" those in which a portion of the kinetic energy of two colliding atoms is expended in raising one of the atoms to an excited state. If, on the other hand, an excited atom loses a portion of its excitation energy during a collision, it is said to undergo a "collision of the second kind." It was demonstrated by Cario and Franck³ that mercury atoms which had been excited by the absorption of radiations of the wave-length 2537Å, a mercury resonance line, can undergo collisions of the second kind with thallium or sodium atoms. This means that during the collision the mercury atom passes some of its excitation energy to the atom with which it collides, raising the latter to an excited state. The excess of energy possessed by the excited mercury atom over that required to excite the thallium or sodium atom is converted into kinetic energy of the atoms separating after the collision. The excited alkali atom then, after a brief period, drops back to its normal state emitting the line corresponding to the energy lost in the transition from the excited state attained as the result of the collision. The effect observed experimentally is that, when a mixture of sodium and mercury vapors is irradiated with a monochromatic ray which is absorbed only by the mercury, the mixture emits a ray characteristic of sodium. Turner found that in processes of this kind, the excited mercury atom usually drops to the longer-lived metastable state before colliding with other atoms, at least under certain conditions of pressure.⁴ Stuart's experiments^{4a} on the quenching of the resonance fluorescence of mercury by radiationless collisions with foreign gas atoms indicated the excited mercury atom to have a larger effective radius than it has in the normal state.

The possibility that such collisions of the second kind of excited atoms with molecules might induce the molecules to enter reactions was soon recognized. Taylor, Marshall and Bates⁵ found that hydrogen could be made to combine with oxygen when the gas mixture which had been bubbled through liquid mercury at the ordinary temperature, is irradiated with the resonance line of mercury

¹ Turner, L. A., *J. Phys. Chem.*, **32**, 507 (1928). For a detailed discussion, see Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge Univ. Press, 1934.

² Klein, O., and Rosseland, S., *Z. Physik*, **4**, 46 (1921).

³ Cario, G., *Z. Physik*, **10**, 185 (1922); Cario, G., and Franck, J., *Ibid.*, **11**, 161 (1922); **17**, 202 (1923).

⁴ See also Donat, K., *Z. Physik*, **29**, 345 (1925); Wood, R. W., *Proc. Roy. Soc. London*, **106A**, 679 (1924).

^{4a} Stuart, H. A., *Z. Physik*, **32**, 262 (1925).

⁵ Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature*, **117**, 267 (1926); see also Senftleben, H., and Rehren, I., *Z. Physik*, **37**, 529 (1926) for the discussion of water vapor.

obtained by the use of a cooled mercury arc. Such a reaction could not be induced by this line in the absence of mercury vapor.⁶ At high rates of gas flow, hydrogen peroxide could be detected as a product of the reaction, and some mercuric oxide formed on the surface of the metal.⁷ Taylor⁸ reviewed the early work on this and many other gas reactions and claimed to have reduced carbon monoxide to formaldehyde, methane and polymerized hydrocarbons by this method. Similar work was reported by Hirst.⁹ Taylor, Marshall and Bates¹⁰ showed that the function of the mercury surface was merely to furnish mercury atoms, the reaction occurring in the vapor phase. Mercury atoms adsorbed on a copper catalyst¹¹ are usually not activated sufficiently in the light of a mercury arc to cause a reaction between hydrogen and ethylene.

In the mercury-sensitized, hydrogen-ethylene reaction, there are formed ethane, methane, propane and butane.¹² Three primary reactions are postulated:

- (1) $H_2 + Hg^* \longrightarrow Hg + 2H.$
- (2) A splitting off of hydrogen from ethylene.
- (3) The opening of the ethylene double bond.

The last reaction is possible since it requires less energy than that corresponding to the 4.9 volts or 112 kcal. of excitation energy of the mercury atom. Bates and Taylor¹³ extended the method to a wide variety of reactions, including many organic compounds. They found the excited mercury atom highly efficient in breaking the linkings, $H-H$, $N-H$ and $O-H$. The decompositions obtained were often many hundreds of times those obtained by exposure of the reactants to the complete ultraviolet spectrum of the mercury arc without the addition of the sensitizer. From this it followed that the energies of these bonds must all be less than 112 kcal., a conclusion substantiated by thermal data. In the breakdown of ammonia, the percentage of hydrogen in the reaction products was found to be greatly in excess of that required had a simple decomposition to the elements occurred. It was therefore, suggested that the reaction occurs in stages, in such a way that some nitrogen-rich substance such as hydrazine can be formed.¹⁴ Mitchell¹⁵ also reported on the fluorescence of ammonia excited by collisions with excited mercury atoms. Bates and Taylor¹⁶ extended the investigation to sensitizations by cadmium vapor, but Bates found that cadmium atoms excited to the 2^3P_1 state did not possess sufficient energy to effect the reaction between hydrogen and ethylene.¹⁷ The possibility of such a reaction can at present be determined directly from the energy-level diagram of the atom proposed as sensitizer and from the thermally known energy requirement for the reaction in question. In general, it has been found to be true that collisions of the second kind are most probable when the

⁶ Dickinson, R. G., *Proc. Nat. Acad. Sci.*, **10**, 409 (1924); Marshall, A. L., *J. Phys. Chem.*, **30**, 34, 1078 (1926).

⁷ See also Bonhoeffer, K. F., and Loeb, S., *Z. physik. Chem.*, **119**, 474 (1926), and Hirst, H. S., and Rideal, E. K., *Nature*, **117**, 449 (1926).

⁸ Taylor, H. S., *Trans. Faraday Soc.*, **21**, 560 (1926).

⁹ Hirst, H. S., *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926); *Chem. Abs.*, **20**, 2459 (1926).

¹⁰ Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature*, **117**, 267 (1926).

¹¹ Ryerson, L. H., *Physics*, **2**, 70 (1932); for a recent summary, Norrish, R. G. W., *Trans. Faraday Soc.*, **35**, 21 (1939).

¹² Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.*, **48**, 389 (1926); **49**, 3131 (1927).

¹³ Bates, J. R., and Taylor, H. S., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); *J. Am. Chem. Soc.*, **49**, 2438 (1927).

¹⁴ See also Dickinson, R. G., and Mitchell, A. C. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

¹⁵ Mitchell, A. G. G., *J. Am. Chem. Soc.*, **49**, 2699 (1927).

¹⁶ Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **50**, 771 (1928).

¹⁷ Bates, J. R., *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

energy of the excited atom can be almost entirely consumed in the excitation of another atom or the disruption of a molecule. Processes in which there is much excess energy of excitation to be converted into kinetic energy are less probable.

Apparatus for effecting gas reactions photosensitized by metal vapors has been patented.¹⁸ Among the reactions for which it was intended was the conversion of water gas into formaldehyde.¹⁹

It is a comparatively simple step from the consideration of these reactions to that of those in which the sensitizer is a molecule rather than an atom. Dhar and Mukerji²⁰ and also Berthoud²¹ discussed the use of chlorine as a sensitizer for the decomposition of ozone, and Taylor and Emeléus²² considered photosensitization by means of ammonia. In such cases, one is dealing with dissociated and not excited molecules. The dissociation products can initiate chain reactions. Details of these processes will be considered in later chapters in dealing with individual reactions.

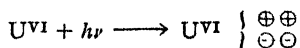
Other Theories of Photosensitization.²³ Many instances of photosensitization by solids, as zinc oxide, have been described. Colloidal hydrous stannic oxide or ignited stannic oxide is said to enable sunlight to effect the oxidation of ammonia to nitrite or the reduction of nitrates to nitrites, and also to decolorize such dyes as methyl violet, methylene blue or brilliant green. The yields are very small.²⁴

Irradiation of a crystal of cadmium sulfide so alters the potential of its surface field as to lessen its ability to adsorb phenolphthalein from an alcoholic solution.²⁵

A novel theory of sensitized photolysis, developed by Baur²⁶ to explain the action of zinc oxide or uranyl salts in promoting various photochemical processes, has also been extended to cover certain cases of sensitization by dyes. The sensitizer is thought to become on absorption of light a polarized molecule, comparable to the two electrodes of an electrolytic cell.²⁷ In the case of uranyl salts, the absorption process is written:



In a more general form, it may be written:



The displaced electrons return to their original state through a "molecular electrolysis," the energy for which is derived from the increase in the potential energy of the valence electrons attained during the process of light absorption. The

¹⁸ I. G. Farbenindustrie A.-G., British P. 307,406, Feb. 11, 1927; 307,521, Feb. 11, 1927; *Chem. Abs.*, 23, 5112 (1929).

¹⁹ See also Frankenburger, W., and Steigerwald, C., German P. 513,461, Nov. 21, 1926; *Chem. Abs.*, 25, 1303 (1931); Frankenburger, W., and Mayrhofer, K., German P. 528,040, Sept. 4, 1927 (to I. G. Farbenindustrie); Buttolph, L. J., U. S. P. 1,844,421, Feb. 9, 1932 (to General Electric Vapor Lamp Co.).

²⁰ Dhar, N. R., and Mukerji, B. K., *Trans. Faraday Soc.*, 21, 645 (1926).

²¹ Berthoud, A., *Trans. Faraday Soc.*, 21, 554 (1926).

²² Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, 52, 2150 (1930).

²³ Work on photosensitization has been reviewed by Farkas, L., Haber, F., and Harteck, P., *Z. Elektrochem.*, 36, 711 (1930) and by Livingston, R., *J. Chem. Ed.*, 11, 400 (1934).

²⁴ Varadanam, C. I., and Rao, G. G., *Current Sci.*, 7, 231 (1938); *Chem. Abs.*, 33, 1598 (1939).

²⁵ Hedvall, J. A., and Gohn, G., *Nature*, 143, 330 (1939); note also Vartanyan, A. T., *J. Gen. Chem. (U.S.S.R.)*, 8, 1098 (1938); *Chem. Abs.*, 33, 4878 (1939).

²⁶ Baur, E., *Helv. Chim. Acta*, 1, 186 (1918); 12, 793 (1929); *Z. Elektrochem.*, 34, 595 (1928).

²⁷ Burgher, K., *Z. wiss. Phot.*, 24, 393 (1927). Baur has attempted to use his concept in explaining the assimilation of carbon dioxide by plants, *Helv. Chim. Acta*, 20, 387 (1937).

positive and negative poles in the molecule act as anode and cathode in a kind of molecular electrolysis. Using silver nitrate as cathodic depolarizer and sucrose, glycine or glycerol as anodic depolarizer, the sensitizing action of the following dyes has been studied: rhodamine B, eosin, safranin-G, phenosafranin, fluorescein, methyl violet, chromotrope-2R. The photolysis results in the separation of silver and the concomitant formation of oxidation products. Some silver was liberated in the binary systems, silver nitrate-dye, silver nitrate-sucrose, but a larger amount was set free in the ternary systems composed of dye and depolarizers.

The sensitized photolysis very soon reaches a stationary state, apparently owing to the formation of a new anodic depolarizer which begins to compete with the existing depolarizer. The experiments with glycine and glycerol show that these substances can be further oxidized in this manner.

The investigation of Burgher lends support to an inner polarization mechanism for sensitization. It may also be noted that in certain instances photosensitization may be ascribed to the absorption of light by complexes formed between the sensitizer and one of the reactants, neither of the components absorbing alone. Instances will be discussed in the treatment of specific reactions.

The ability of a series of complex cobalt salts to sensitize the oxidation of potassium iodide, pyrogallol, benzidine, *p*-phenylenediamine and other substances when both the substrate and sensitizer are irradiated, usually by the 3660 Å line, was studied by Watanabe.²⁸ Of the nitro-cobaltic compounds, those which had two nitro-groups attached to the nucleus were most strongly affected by light. The oxidizing ability of the croceo-chloride (*trans*) was more photosensitive than that of the flavo-chloride (*cis*), which showed oxidizing action even in darkness. The magnitude of the photoactivity of nuclei of the type $\text{Co}(\text{NH}_3)_5\text{X}$ was influenced by the coordinated acid radical in the order $\text{SCN} > \text{NO}_2 > \text{CO}_3 > \text{Cl}$.

Mukerji and Dhar²⁹ find that in photosensitized systems there is a marked increase in the light absorption not found in systems they believe to be photo-inhibited. Dhar and Bhattacharya³⁰ suggest that the presence of a second reactant may sensitize molecules to radiation of longer wave-length.

Relation of Fluorescence to Sensitization.³¹ An understanding of the nature of the photodynamic action of many fluorescent dyes upon living organisms (Chapter 42) and of the function of chlorophyll in the photosynthesis of carbohydrates (Chapter 43) depends upon the advances in our knowledge of the mechanism of photosensitization by these fluorescent substances. A much discussed recent question is whether the reactions effected by these agents are to be ascribed to their fluorescence or whether this property is merely an incidental phenomenon which may even lessen their effectiveness as sensitizers. Viale³² believed that, since the additions of foreign substances to dyes lessened both their fluorescence and their effectiveness as sensitizers, the fluorescence was in some manner responsible for their sensitizing action. West, Müller and Jette,³³ however, pointed out that any addition of ions in solution which tends to destroy an activated molecule will simultaneously destroy the ability of that molecule to impart its energy to a chemical reaction or to emit it as fluorescence. The addition of reactants, which

²⁸ Watanabe, A., *Iwata Inst. Plant Biochem. Publ.*, 2, 129 (1936); *Chem. Abs.*, 30, 6650 (1936).

²⁹ Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, 5, 411 (1928); *Chem. Abs.*, 23, 40 (1929).

³⁰ Dhar, N. R., and Bhattacharya, A. K., *J. Indian Chem. Soc.*, 11, 33 (1934); *Brit. Chem. Abs.*, 1934A, 496.

³¹ For earlier theoretical discussions, see Steigmann, A., *Kolloid-Z.*, 44, 173, 248 (1928); *Z. wiss. Phot.*, 26, 299 (1929).

³² Viale, G., *Arch. ital. biol.*, 73, 19 (1924); *Chem. Abs.*, 19, 2346 (1925).

³³ West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, 121A, 294, 299, 313 (1928).

may remove excitation energy by collisions of the second kind and thus render it available to the reaction, also decreases the fluorescence. Many believe that the primary process in the reactions underlying photodynamic oxidations by dyes is the quenching of their fluorescence in solution by reactants.³⁴ Others, however, believe that, in general, photosensitized reactions in solution proceed rather by the use of energy absorbed in linkings or parts of the sensitizing molecule which never appears as fluorescence.³⁵

The mechanism of the fluorescence of dyes and of its quenching has been the subject of much recent work. The advances in this, possibly the phase of photochemistry at present the most rapidly developing, have been summarized in a recent discussion of the Faraday Society.³⁶ Although the subject is still in a somewhat confused state, certain concepts have emerged.

Pringsheim³⁷ points out that fluorescence is the exception rather than the rule in organic molecules, most substances with large light absorption converting the energy thus acquired into heat by little understood mechanisms. He finds little known regarding the conditions that must be met in order that a substance in a condensed phase may fluoresce. One view is that, since the absorption of fluorescent dyes lies in the visible region, the quanta gained by absorption are too small to initiate quenching processes and, therefore, can only be lost by fluorescence. This seems inadequate since a large number of dyes with visible absorption are not fluorescent. In the rare earths and uranyl compounds, the narrowness of the absorption bands has been held to indicate that the electron transfer process is well protected against fluorescence. Although this seems true also of chlorophyll and porphyrins, it does not apply to many dyes, such as uranin or tryptaflavin, so that it is improbable that there can be a definite correlation between the fluorescence of a compound and the width of its absorption bands. Furthermore, there seems to be no parallelism between the electrical conductivity of a dye and its fluorescence, although it is true that, as in the case of fluorescent indicators, the absorption spectra and fluorescence may vary with the state of ionization of the dye. Weiss³⁸ believes that all organic molecules with strong fluorescence have conjugated band systems in which the excitation energy is not easily transformed into heat, or in other words, that there is no coupling between free electrons of these systems and the vibrations of the heavy particles. Mumm³⁸ regards the fluorescent substance as an intermediate state (resonance form) between two end structures. Absorption raises an electron to an excited state from which it drops to one of the end states with the appearance of fluorescence. This end structure then passes to the intermediate state with evolution of heat. He has applied this theory, developed for N-methyl- α -pyridones, to the fluorescence of barium platino-cyanide and to uranyl salts.

A number of studies have been concerned with the measurement of the fluorescence efficiency of dyes and other substances. Some materials, as solid anthracene, have high efficiencies approximating unity. In various solvents, however, anthracene has maximal efficiencies which vary from 0.28 to 0.01. Bowen and Norton³⁹

³⁴ Noack, K., *Naturwiss.*, 14, 383 (1926); *Chem. Abs.*, 20, 2521 (1926); 21, 2011 (1927); *Biochem. Z.*, 183, 144 (1927); Gaffron, H., *Biochem. Z.*, 179, 157 (1926).

³⁵ Shpol'skii, E., and Sheremet'ev, G., *J. Phys. Chem. (U.S.S.R.)*, 8, 640 (1936); *Chem. Abs.*, 31, 2100 (1937).

³⁶ *Trans. Faraday Soc.*, 35, 15 (1939).

³⁷ Pringsheim, P., *Ibid.*, 35, 28 (1939).

³⁸ Mumm, O., *Ber.*, 72B, 29 (1939). For an earlier discussion of theories of fluorescence, see Perrin, F., *Ann. Physique*, 12, 169 (1929).

³⁹ Bowen, E. J., and Norton, A., *Trans. Faraday Soc.*, 35, 44 (1939).

find that the fluorescence efficiency F depends on the nature of the fluorescent substance, the solvent, concentration of solute, temperature and concentration c of quencher. It may be expressed by $F = \frac{k_1}{1 + k_2 C}$ in which k_1 and k_2 are constants.

Many processes tend to lower the efficiency in solution. Some, such as an inner filtering action of some solute or of the solvent, or the formation of non-fluorescent compounds with the solvent, or the formation of aggregates,⁴⁰ do not appear to be related to true quenching processes. The progressive introduction of halogens into such a dye as fluorescein diminishes the fluorescence; for this the somewhat misleading term "internal quenching" has been suggested.

True quenching of fluorescence in solution refers to a process in which the excitation energy absorbed by a certain percentage of the absorbing molecules may be transferred to other molecules before it can be emitted as light.⁴¹ Two types have been distinguished. The quenching is said to be static when the quenching molecule is within the sphere of action of the fluorescent molecule during the absorption process. When the quencher must diffuse toward the excited molecule during its lifetime, the quenching is said to be diffusional. Many strong quenchers of dye fluorescence act in this manner.

The quencher may be an inorganic ion, as studied by West, Müller and Jette,⁴² a foreign molecule as oxygen, or even other molecules of the fluorescent substance. If the latter, the process of quenching (self-extinction) generally causes the fluorescence intensity to decrease with an increasing concentration of the dye. Self-extinction may be regarded as due to collisions of the second kind between like molecules. Kautsky,⁴³ however, claims that this is incorrect and that self-extinction is due to a lengthening of the life of the excited molecules. This view is based chiefly upon observations of fluorescent solids which show increased phosphorescence with decreased fluorescence. Kautsky claims that in liquids long-lived states may be produced, although the phosphorescence lasts but 10^{-8} sec. because of the greater ease of the conversion of excitation energy into thermal energy. Concentration quenching occurs at such low concentrations as 10^{-4} mole per liter in the case of anthracene solutions. Pringsheim points out that this could scarcely be accounted for by energy resonance between excited and unexcited molecules. He suggests that it may more likely be related to a utilization of part of the energy in some photochemical change, the excess being converted into heat. In the case of anthracene, the reaction is the formation of dianthracene (Chapter 26). The self-extinction of fluorescence is also encountered in the case of the photochemical reactions of other hydrocarbons with condensed ring systems.

Other molecules, *e.g.*, non-fluorescent dyes, with absorption bands overlapping those of the fluorescent substance, act as strong quenchers. Many antioxidants,⁴⁴ phenols, amines and the iodide ion act as quenchers. In such cases, little is known of the mechanism of quenching. Most quenchers act only after many collisions and in some cases it is believed that the quenching is stepwise. Since the temperature has little influence, no activation seems necessary.

In the Faraday Society discussion, D. D. Eley suggested that the magnetic

⁴⁰ Kortüm, G., *Z. physik. Chem.*, **33B**, 1 (1936); **34B**, 255 (1936); Lewschin, W. L., *Acta Physicochim. U.S.S.R.*, **2**, 221 (1935); *Chem. Abs.*, **29**, 7798 (1935).

⁴¹ Franck, J. M., and Wawilow, S. J., *Z. Physik.*, **69**, 100 (1931); Sveshnikov, B., *Acta Physicochim. U.R.S.S.*, **3**, 257 (1935); **4**, 453 (1936); **7**, 755 (1937); *Chem. Abs.*, **30**, 3327 (1936); **31**, 5681 (1937); **32**, 4880 (1938).

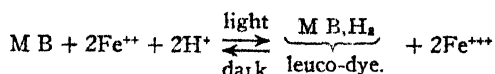
⁴² West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, **121A**, 294, 299, 313 (1928).

⁴³ Kautsky, H., and Merkel, H., *Naturwiss.*, **27**, 195 (1939).

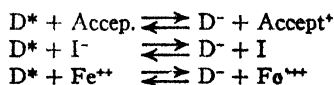
⁴⁴ Perrin, J., *Compt. rend.*, **184**, 1097 (1927); Privault, *Ibid.*, **184**, 1120 (1927).

effect of such paramagnetic ions as Fe^{++} , Ni^{++} , Cu^{++} may quench the fluorescence of porphyrins by a magnetic predissociation process. Halide ions might also quench dyes by a predissociation process induced by their electric fields did their hydration envelopes not prevent the ions from approaching closely enough. Weiss, however, showed that strong magnetic fields do not affect the fluorescence of dye solutions, and believed the halide ions to act by a radiationless transfer of an electron from the ion to the excited dye. This theory may be compared with the view of Hachkowskiĭ and Terenin⁴⁵ that molecules adsorbed on fluorescent solids quench by taking up free electrons from the solids to form negative ions.

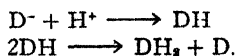
Weiss⁴⁶ has developed his theory in considerable detail and employed it to interpret a number of experimental observations. The irradiation with a 1500-watt carbon arc of a methylene blue solution in the presence of the ferrous ion, causes a bleaching which is reversed when the irradiation ceases.



Although the iodide ion had no similar effect on methylene blue, it did cause a bleaching action, proportional to the square root of the light intensity, on Lauth's violet and a slight one on eosin. Weiss holds that when an excited dye molecule D^* collides with an acceptor molecule or ion which has an electron in a level corresponding to that left vacant by the electronic shift in the dye excitation, the electron passes to the excited dye, forming the non-fluorescent excited D^- .



A quantum mechanical resonance between the states (D^* , Accep) and D^- , Accep⁺ is assumed. The dye molecule with the electron thus acquired may then on combination with a proton form a semiquinone DH, two molecules of which react to form the leucobase and oxidized dye.



It was possible to develop mathematical relations between the relative effectiveness of various halogen ions in quenching dye fluorescence and their electron affinities.⁴⁷

The reactions described may also be used to explain the dye-photosensitized oxidation of larger quantities of ferrous ion, iodide ion or other acceptor, since when the semiquinone or leucobase has been formed, it can be reoxidized thermally to the dye by the air and thus be made capable of oxidizing more of the acceptor.

It will be noted that this theory takes no account of any effect which oxygen itself may have upon the fluorescence of the dye.⁴⁸ It has, however, been demonstrated that the fluorescence of chlorophyll or hematoporphyrin can be quenched by molecular oxygen, and cannot be quenched by acceptors, such as thiosinamine or

⁴⁵ Hachkowskiĭ, V., and Terenin, A., *Acta Physicochim. U.R.S.S.*, **7**, 521 (1937).

⁴⁶ Weiss, J., *Trans. Faraday Soc.*, **32**, 1331 (1937); **35**, 48 (1939); *Nature*, **135**, 648 (1934); **136**, 794 (1935); Weiss, J., and Fishgold, H., *Z. physik. Chem.*, **32B**, 135 (1936); *Nature*, **137**, 71 (1936).

⁴⁷ See also Weber, K., *Z. physik. Chem.*, **30B**, 69 (1935).

⁴⁸ Schneider, E., *Z. physik. Chem.*, **28B**, 311 (1935).

isoamylamine. Such observations led Kautsky⁴⁹ to propose a different theory of photosensitized oxidations according to which it is assumed that collision with an excited dye molecule raises an oxygen molecule into a metastable excited state. Gaffron⁵⁰ disagreed with this (for further details see Chapter 44) and Franck and Levi⁵¹ suggested that the HO_2 molecule may be formed in the quenching process and subsequently react with an acceptor. Weiss suggests the possibility of the O_2^- ion instead, believing its formation especially likely in the case of the collision of an oxygen molecule with an absorbed and excited dye such as trypanflavine.⁵²

In his most recent work, Kautsky⁵³ studies particularly the phosphorescence of dyestuffs adsorbed on silica or alumina gels and maintained in an evacuated vessel. The phosphorescence is said to be quenched by oxygen independently of its pressure down to a few thousandths of a mm. The quenching of the fluorescence, however, is said to depend upon the oxygen pressure. Kautsky interprets these experiments as favoring the formation of metastable oxygen molecules, since he could detect their diffusion by the following method. A mixture of fine grains of silica gel with adsorbed sensitizer and larger grains of silica gel with adsorbed leuco-methylene blue became blue when the oxygen pressure was made just small enough to quench the fluorescence of the sensitizer. When both the sensitizer and the acceptor are adsorbed on the same surface, the diffusion path is shortened and in light the color becomes blue at pressures up to one atmosphere. Such a mixed adsorbate is regarded as representing a transition to the conditions encountered in solution. An essential feature of Kautsky's theory is the phosphorescence, some oxygen-free solutions of sensitizers being reported to exhibit light for as long as 10^{-2} sec., after illumination, whereas the life of the usual excited state which causes fluorescence is only of the order of 10^{-8} sec. This phosphorescence, the yield of which is small, is thought to occur only in regions where there is slight association of the dye molecules. This afterglow is thought to be due to metastable excited states of dyes capable of causing but weak fluorescence. The afterglow can be demonstrated by the addition to 20 cc. of acetone of two to four drops of a 0.006 molar solution of any such efficient photosensitizers of oxidation as isoquinoline red, benzoflavine, eosin, hematoporphyrin, chlorophyll, erythrosin, phloxin or rose Bengal.⁵⁴ Strongly fluorescent compounds do not exhibit it under these conditions. A very small concentration of oxygen inhibits the afterglow, but the oxygen acceptors, thiosinamine and isoamylamine, have no effect.

Scheibe⁵⁵ suggests that in solution certain dyes may occur as polymers of several hundred molecules. The polymer may absorb many quanta simultaneously. This energy may be lost by fluorescence or by collision with a foreign molecule which may thus acquire a very large number of quanta, resulting in the formation of short-lived intermediate products at energy levels which could never be attained by the direct absorption of light.

Claims of the existence of a negative photosensitization have been made. Milbauer⁵⁶ observed that in the presence of 0.02, 0.2 or 1.0 mg. of the dyes Nile blue, Brilliant Green, Capri Blue, phenosafranine, fuchsin, pinacryptol green or

⁴⁹ Kautsky, H., and de Bruijn, H., *Naturwiss.*, 19, 1043 (1931); Kautsky, H., *Ber.*, 65, 1762 (1932); *Trans. Faraday Soc.*, 35, 216 (1939).

⁵⁰ Gaffron, H., *Biochem. Z.*, 264, 251 (1933); *Ber.*, 68, 1409 (1935).

⁵¹ Franck, J., and Levi, H., *Naturwiss.*, 23, 229 (1935).

⁵² See Pringsheim, P., and Vogels, H., *J. chim. phys.*, 33, 345 (1936).

⁵³ Kautsky, H., *Trans. Faraday Soc.*, 35, 216 (1939).

⁵⁴ Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, 68B, 152 (1935).

⁵⁵ Scheibe, G., *Naturwiss.*, 25, 795 (1937).

⁵⁶ Milbauer, J., *Chem. Listy*, 29, 267 (1935); *Phot. Korr.*, 71, 94; *Chem. Abs.*, 30, 1661 (1936).

methylene violet per 10 cc., the rate of decomposition of an active methanol solution containing 28.2 gm. per liter of sodium N-chloro-*p*-toluenesulfonamide is slower than in their absence, when exposed to intense visible light. Since simultaneous experiments with these dye mixtures in darkness did not show a loss of activated chlorine, it was believed that a negative photocatalysis had been demonstrated. In the same range of concentrations, malachite green, pinacryptol yellow and methylene blue did not exhibit this phenomenon, for in darkness they consumed activated chlorine and were themselves decomposed.

A more complete discussion of the phenomena of luminescence and phosphorescence lies beyond the scope of this book, although in some instances ultraviolet radiations may be employed in eliciting these phenomena. Some developments of the earlier work in these fields led to significant work on the nature of the coloration produced in alkali halide crystals by irradiation. These are discussed in Chapter 21. A general discussion of the mechanism of phosphorescence has been given by Pohl.⁵⁷ A phosphor may be defined as an insulating crystalline material into which a minute trace of a highly refracting substance has been incorporated in the molten state. Excitation consists in the liberation of electron by photoelectric effects; luminosity arises from the return of such electrons to the normal state.

Chemoluminescence. This phenomenon represents, in a way, the converse of a photochemical change or of a photosensitized reaction. It is a process in which light is evolved during the course of a chemical reaction; the efficiency is seldom more than 1 per cent. Limitations of space prevent the discussion of this topic. For recent discussions, see Kautsky,⁵⁸ Nichols,⁵⁹ Beutler,⁶⁰ and a report of the National Research Council.⁶¹

PHOTOCHEMICAL REACTIONS IN SURFACES

Recently an attempt has been made to develop the theory that the velocity of photochemical reactions conducted in mono- or multi-molecular layers at the surface of a liquid depends upon the molecular orientation of the absorbing molecules.⁶² Among the reactions studied have been the hydrolysis of stearic anilide spread on half-normal sulfuric acid, the decomposition of α -hydroxystearic acid with liberation of carbon dioxide produced by wave-lengths shorter than 2480 Å, the oxidation and hydrolysis of proteins, etc. The effects of traces of such sensitizers as nickel and copper and of inhibitors as potassium cyanide is, in some cases, pronounced.

On glass of refractive index 1.5, invisible multilayers of barium acid stearate (containing equal parts of stearic acid and barium stearate in each) when irradiated by a high-pressure mercury arc showed interference colors. Five minutes of irradiation of a 48-layer film caused a loss of optical thickness which amounted to one layer.⁶³ The loss continued for several hours after the irradiation had been stopped, finally amounting to more than two layers. A similar change occurs in pure stearic acid layers, but barium stearate shows only one twentieth this loss.

⁵⁷ Pohl, R. W., *Naturwiss.*, **16**, 477 (1928), see also Melville, H. W., *Science Progress*, **33**, 527 (1939); Leverenz, H. W., and Seitz, F., *J. Applied Physics*, **10**, 479 (1939); Symposium on Luminescence, *Trans. Faraday Soc.*, **35**, 2 (1939).

⁵⁸ Kautsky, H., *Trans. Faraday Soc.*, **21**, 591 (1925).

⁵⁹ Nichols, E. L., *J. Opt. Soc. Am.*, **20**, 106 (1930).

⁶⁰ Beutler, H., *Angew. Chem.*, **45**, 249 (1932); Beutler, H., and Polanyi, M., *Z. Physik*, **47**, 379 (1928).

⁶¹ *Bull. Nat. Research Council*, **59**, 30 (1927).

⁶² Mitchell, J. S., *J. Chem. Physics*, **4**, 725 (1936); **5**, 83 (1937); Mitchell, J. S., Rideal, E. K., and Schulman, J. H., *Nature*, **139**, 625 (1937); Rideal, E. K., and Mitchell, J. S., *Proc. Roy. Soc. London*, **159A**, 206 (1937).

⁶³ Schaefer, V. J., *Science*, **89**, 465 (1939).

It is believed that radiations of 2300-2700A split the molecules of stearic acid at the attachment of the carboxyl group.

PHOTOCHEMISTRY AND OPTICAL ACTIVITY

There have been many attempts to prepare optically active substances by methods such that the form with one configuration results in larger amount than its antipode. One of the first successful experiments was performed in 1930 by Kuhn and Knopf.⁶⁴ It involved the use of circularly polarized light in causing the decomposition of α -azidopropiondimethylamide. This compound has an absorption band at about 2900A with a strong anisotropic factor of 0.02-0.03.⁶⁵ When acted upon in hexane solution by circularly polarized light of this wave-length, it undergoes decomposition of the azido-group, one stereoisomer being decomposed to a greater extent than the other. This is because the difference between the absorption coefficients of the compound for right and left circularly polarized light is, as stated, about 2 to 3 per cent. From the amount of nitrogen liberated, it was shown that the reaction follows approximately the Einstein equivalence law. The unchanged dimethylamide can be separated from the reaction products by distillation. When 40 per cent of the original racemic compound had been decomposed, the remainder showed in a 10-cm. polariscope tube a rotation of $+0.78^\circ$ when the irradiation had been conducted with *d*-circularly polarized light and of -1.04° when *l*-circularly polarized light had been used. The order of magnitude of these effects was in agreement with theoretical predictions. Kuhn, with Braun⁶⁶ had made earlier similar observations on ethyl α -bromopropionate in which near ultraviolet bands powerfully influence the optical activity.

Important earlier contributions to the field of asymmetric synthesis employing circularly polarized light and magnetic fields were made by Cotton.⁶⁷ In these experiments, active molecules were not, however, produced, as there resulted only an active arrangement of the molecules in a medium.⁶⁸ Studies of the photodichroism and photoanisotropy of light-sensitive solid layers of a gelatin photographic emulsion have been made by Weigert.⁶⁹ The primary action in induced photodichroism is assumed to be the deformation of micelles held together by van der Waals forces. The form of the spheres detached within the micelles depends on the wave-form of the exciting light.⁷⁰

There have been other recent attempts to obtain a total asymmetric synthesis. Davis and Haggie⁷¹ reported the production of optically active trinitrostilbene dibromide by the photobromination of 2,4,6-trinitrostilbene by circularly polarized light of wave-lengths 3600 to 4500A. As solvents, they used carbon tetrachloride, benzene, glacial acetic acid and nitrobenzene. The last was the most suitable. In every case the reaction mixture assumed an optical activity which increased to a maximum and then decreased slowly and finally disappeared as the reaction

⁶⁴ Kuhn, W., and Knopf, E., *Naturwiss.*, 18, 183 (1930); *Z. physik. Chem.*, 7B, 292 (1930); *Ber.*, 63B, 190 (1930).

⁶⁵ The theory of the relation between circular dichroism and optical rotatory power within and without absorption bands previously developed by Kuhn, W., *Z. physik. Chem.*, 4B, 14 (1929) led to this work.

⁶⁶ Kuhn, W., and Braun, E., *Naturwiss.*, 17, 227 (1929).

⁶⁷ Cotton, A., *Compt. rend.*, 189, 657 (1929).

⁶⁸ See also Zocher, H., and Koper, K., *Z. physik. Chem.*, 132, 295, 302, 313 (1928); Bruhat, G., *Bull. soc. chim.*, 47, 251 (1930).

⁶⁹ Weigert, F., *Z. physik. Chem.*, 3B, 377, 389 (1929); 4B, 83 (1929). See also Chapter 21.

⁷⁰ Weigert, F., *Z. physik. Chem.*, 10B, 241 (1930); Ghosh, J. C., *J. Indian Chem. Soc.*, 16, 51 (1938); *Chem. Abs.*, 33, 5744 (1939).

⁷¹ Davis, T. L., and Haggie, R., *J. Am. Chem. Soc.*, 57, 377 (1935).

proceeded to completion. Since the product on standing, whether in ordinary or in polarized light, loses its optical activity and since this cannot be restored by further exposure to polarized light, it was inferred that optical activity arises at the moment of the synthesis of the compound. The degree of rotation secured, although small (0.04°), was beyond the limit of error of the observations. The reaction is a chain, initiated by excited bromine atoms in which activated trinitrostilbene molecules may or may not take part. In diffused daylight or in unpolarized light, the reaction failed to form optically active material. Optically inactive trinitrostilbene dibromide is not rendered active by exposure of its solutions in nitrobenzene to circularly polarized light. In these experiments, the circularly polarized light was obtained by reflecting the light of a glass-enclosed mercury arc filtered through blue cobalt glass at the polarizing angle from a plate of black glass and by passage through a thin sheet of mica. No optically active product could be obtained by the use of circularly polarized light of wave-length 5890-5896Å. The formation of optically active material was also observed when chlorine reacted with trinitrostilbene in nitrobenzene solution in circularly polarized light of wave-lengths between 3600 and 4500Å. The reaction was much faster than in the case of bromine but no greater activity could be obtained. Maximum rotations were obtained in about 45 minutes.

Attempts of this sort had been previously made by Ghosh and Purkayastha⁷² in the bromination of stilbene and of cinnamic acid, but the formation of optically active materials was not described. They found for the same intensities, ordinary light and plane polarized light to be equally effective, and circularly polarized light slightly less so. In the decomposition of potassium manganioxalate, however, it was slightly more effective than either non-polarized or plane-polarized light.⁷³

By irradiating methyl (4-methylphenyl) (*p*-ethylphenyl)trimethylmethane with circularly polarized light of 4300Å while introducing chlorine at 0° , Karagunis and Drikes⁷⁴ claimed to have obtained an optical rotation of 0.1° . When light (5890Å) which lies within the absorption band was used, the opposite rotation appeared.

Observations by Baly and Semmens⁷⁵ regarding the action of plane polarized light in hydrolyzing starch in plant leaves stimulated a large amount of work in which it was attempted to show that polarized light is more effective than ordinary light in effecting various photochemical reactions. Whatever may subsequently be found in regard to the action of plane polarized light upon substrates the molecules of which are definitely oriented in surface layers, in solids or in biological structures, there is no reason to expect it to be more effective than ordinary light of equal intensity in effecting photochemical reactions in solutions in which the substrate molecules have a random orientation. It has been shown by Bhatnagar, Anand and Gupta⁷⁶ that no differences are to be observed in the photochemical reactions by polarized and ordinary light between diammonium oxalate and mercuric chloride or in the decomposition of alkaline hydrogen peroxide.

Nevertheless, it has been claimed⁷⁷ that polarized light produces changes in the

⁷² Ghosh, J. C., and Purkayastha, R. M., *Quart. J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926).

⁷³ Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3**, 127 (1926); *Chem. Abs.*, **20**, 3646 (1926).

⁷⁴ Karagunis, G., and Drikes, O., *Naturwiss.*, **21**, 607 (1933); *Chem. Abs.*, **28**, 144 (1934).

⁷⁵ Baly, E. C. C., and Semmens, E. S., *Proc. Roy. Soc. London*, **97B**, 250 (1924).

⁷⁶ Bhatnagar, S. S., Anand, H. L., and Gupta, A. W., *J. Indian Chem. Soc.*, **5**, 49 (1928); *Chem. Abs.*, **22**, 3840 (1928). Zhalkovskii, B. G., *Bull. biol. med. exptl. U.R.S.S.*, **5**, 493 (1938); *Chem. Abs.*, **33**, 2544 (1939). See also Bhatnagar, S. S., Lal, R. B., and Mathur, K., *Nature*, **118**, 11 (1926) for physiological effects claimed to be due to polarized light.

pharmacological properties of a number of drugs not produced by irradiation with non-polarized light. Irradiation of tincture of digitalis with polarized light was said to produce a deterioration as shown by a weakened pharmacological action. When ultraviolet light is used a further change or decomposition occurs and the tincture becomes more poisonous. With digitalis, it was claimed that circularly polarized light produced even greater deterioration than did plane polarized light. Macht and Krantz⁷⁸ stated that in these experiments the test and control solutions were simultaneously irradiated with polarized and non-polarized light of equal intensity.

On the other hand, Dailey and Benedict⁷⁹ were unable to show that polarized light had any selective action in the decomposition of cocaine hydrochloride, when irradiation times of from one to twelve hours were employed. This is at present generally believed to be true of photochemical reactions of substances under conditions in which they are capable of free and random orientation. Other workers to deny the claims for a special effectiveness of polarized light have been Bunker and Anderson⁸⁰ and Bond and Gray.⁸¹

PHOTOTROPY

This term refers to a change in color suffered by a solid on exposure to light, which is slowly reversed when the solid is subsequently kept in darkness. It was first observed, named and extensively investigated by Marckwald.⁸² It is exhibited by over two hundred substances, but as yet little quantitative work has been done. An interesting feature is the occurrence of phototropic fatigue. 3,5-dibenzoyl-2,4,4,6-tetraphenyltetrahydropyran, which is colorless in the dark, becomes violet on exposure to light, especially that of short wave-lengths. It again becomes colorless after some hours or days in darkness. After ten such colorations and decolorations, however, it loses its phototropic properties and its melting point falls from 235-6° to 225°C.⁸³ In solution, it is insensitive to light, and the colored form when dissolved yields colorless solutions. An occasional instance of phototropy in solution has, however, been reported. Singh⁸⁴ observed a green color to develop in chloroform solutions of α -naphthylaminocamphor on exposure to direct sunlight, followed by a much slower reversal in darkness. The coloration was accompanied by a large increase in optical rotation. The addition of a trace of sodium ethoxide prevented the appearance of the green color. The results were tentatively attributed to the formation of a compound from the keto and enol modifications.

The phototropy of inorganic compounds of the type 2HgS.HgX_2 or 2HgS.HgX has been attributed⁸⁵ to their dissociation into the simple component salts, recombination occurring in darkness with the reëmission of radiant energy.

⁷⁷ Macht, D. I., and Anderson, W. T., Jr., *J. Am. Chem. Soc.*, **49**, 2017 (1927).

⁷⁸ Macht, D. I., and Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **16**, 106 (1927).

⁷⁹ Dailey, H. T., and Benedict, H. C., *J. Am. Chem. Soc.*, **51**, 808 (1929).

⁸⁰ Bunker, J. W. M., and Anderson, E. G. E., *J. Biol. Chem.* **77**, 473 (1928).

⁸¹ Bond, W. R., and Gray, E. W., *J. Pharm. Exp. Therap.*, **32**, 351 (1928). See also for further details of the controversy, Jones, W. N., *Ann. Botany*, **39**, 651 (1925); Baly, E. C. C., and Semmens, E. S., *Nature*, **116**, 817 (1925); Semmens, E. S., *Plant Physiol.*, **1**, 201 (1926); *Nature*, **117**, 821 (1926); Lord Rayleigh, *Nature*, **117**, 15 (1926); Navez, A. E., and Rubenstein, B. B., *J. Biol. Chem.*, **80**, 503 (1928).

⁸² Marckwald, W., *Z. physik. Chem.*, **30**, 140 (1899). For reviews, see Gallagher, P., *Bull. soc. chim.*, **29**, 683 (1921) and Chalkley, L., Jr., *Chem. Rev.*, **6**, 217 (1929). Note also Bhatnagar, S. S., Kapur, P. L., and Hashmi, M. S., *J. Indian Chem. Soc.*, **15**, 573 (1938); *Chem. Abs.*, **33**, 3698 (1939).

⁸³ de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).

⁸⁴ Singh, B. K., *Quart. J. Indian Chem. Soc.*, **1**, 45 (1924); *Chem. Abs.*, **19**, 935 (1925).

⁸⁵ Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929).

PHOTOELECTRIC PHENOMENA

In 1839, Becquerel⁸⁶ discovered that when one of two platinum or silver electrodes in dilute sulfuric acid is illuminated, an electromotive force is set up by the cell. That the conductivity of certain substances, notably selenium, is affected by light was, according to Bidwell⁸⁷ discovered by Willoughby Smith in 1873. In attempting to explain an observation by Hertz⁸⁸ that ultraviolet illumination of a spark gap permits the passage of a longer spark, Hallwachs⁸⁹ discovered the emission of negative electricity from a surface irradiated by ultraviolet rays. As pointed out by Hughes and DuBridge,⁹⁰ these three phenomena are separate manifestations of photoelectric processes, which all depend upon the ability of light to release electrons from matter.

Historically, the photoelectric effect is of the greatest importance, since it was the study of this phenomenon which enabled Einstein⁹¹ to reveal the fact that the interaction between matter and radiation must be explained in terms of quanta of radiation. The theoretical structure of modern photochemistry is based upon his introduction of the concept which led to the logical development of the photochemical equivalence law. On the other hand, the actual occurrence of a photoelectric effect as a part of the mechanism of photochemical processes is relatively unusual. That air and other gases may be ionized by ultraviolet radiations has long been recognized⁹² and at one time it was believed that photoionization might play an important role in photochemical processes. But when the amounts of energy required to ionize the molecules of various gases became known, it became evident that the wave-lengths corresponding to ionization are generally far shorter than those required to bring about most photochemical processes. Only rays passing through fluorite are able to ionize most gases. The required thresholds range from 1300Å for nitric oxide to 760Å for nitrogen, the halogens having the values chlorine, 940Å, bromine, 970Å, and iodine, 1230Å.⁹³

Many investigations have been made of the effects of illumination upon the electrodes of electrolytic or voltaic cells, but these lie beyond the scope of this work.

⁸⁶ Becquerel, E., *Compt. rend.*, **9**, 145, 561 (1939); for a recent review, see Stora, C., *J. chim. phys.*, **34**, 536 (1937).

⁸⁷ Bidwell, S., *Phil. Mag.*, **20**, 178 (1885).

⁸⁸ Hertz, H., *Ann. Physik*, **31**, 983 (1887).

⁸⁹ Hallwachs, W., *Ann. Physik*, **33**, 301 (1888).

⁹⁰ Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," New York, McGraw-Hill Book Co., 1932.

⁹¹ Einstein, A., *Ann. Physik*, **17**, 132 (1905).

⁹² Thomson, J. J., *Proc. Cambridge Phil. Soc.*, **14**, 417 (1907); *Chem. Abs.*, **2**, 1656 (1908).

⁹³ See Mackay, C. A., *Phil. Mag.*, **46**, 828 (1923); Morris, J. C., Jr., *Phys. Rev.*, **32**, 456 (1928); Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," p. 274, New York, McGraw-Hill Book Co., 1932.

Chapter 17

Reactions of Inorganic Gases: Hydrogen Halides

In Chapter 14 it was shown that a knowledge of the spectrum of a gas is essential to comprehending the reactions which it may undergo under the influence of radiations. Even when apparatus capable of revealing the finer structure of the molecular spectra is not available, crude spectrographs may furnish an indication of the wave-length regions within which the gas absorbs and will therefore give some indication of the regions within which photochemical reactions can occur. A brief discussion of the manner in which absorption measurements are made will first be given. Then in the discussions of the individual reactions, the absorption spectrum of each of the components will be described in order that the findings of spectroscopy as to the nature of the possible primary processes may furnish a guide for a critical appraisal of the various speculations proposed in explanation of the reported observations on the kinetics of the reactions.

THE MEASUREMENT OF ULTRAVIOLET ABSORPTION SPECTRA OF GASES OR LIQUIDS

Since this is not a text of laboratory procedure, only principles and not details of technique will be mentioned. In general, the methods are similar to those commonly employed in the visible region. Ultraviolet light, from a spark source or hydrogen discharge tube, is divided into two parallel paths, one of which passes directly into the spectrograph; the other passes through a cell containing the gas or the solution the absorption of which is to be measured. (If the absorption of a solution is being studied, the first beam should pass through a cell containing the pure solvent.) The two spectra are then photographed side by side. Several exposures are made on adjacent portions of the photographic plate, the intensity of the comparison beam being varied to a known extent in each. Methods employed in photometers for decreasing the intensity of the comparison beam include the interposition of rotating sectors which vary in known manner the duration of intermittent exposures, the use of wire screens¹ or calibrated platinum wedges deposited on quartz, Nicol polarizing prisms or variations of the aperture admitting the comparison beam (Spekker method of Adam Hilger, Ltd.). It would theoretically be best to secure the variation in intensity by varying the distance from the source, but this is not feasible when a photographic method is employed and it has rarely been used in other methods.²

In each of the series of double spectra, however obtained, there are located (visually or microphotometrically) the wave-length regions at which there is agreement between the intensity of the light passing through the absorption cell and that coming directly from the source. The wave-lengths corresponding to various positions along the spectrum are determined by a simultaneously photographed scale embodied in the instrument or located by the use of known lines of the source as landmarks. Most of the methods in common use, particularly for

¹ Winther, C., *Z. wiss. Phot.*, **22**, 125 (1923); Landsberg, G. S., *Z. Physik*, **46**, 106 (1927).

² Schaefer, K., *Z. angew. Chem.*, **33**, 25 (1920).

work with solutions, involve merely a direct visual matching of the intensities upon the photographic plate variously illuminated.

A method in which the light intensity was kept constant and the path of absorbent traversed, or the concentration of the absorbing solution, was varied, was introduced by Henri.³ Refinements in this method have been introduced by de Lazlo.⁴ A simple method employing only a quartz spectrograph and no photometer has been employed by Loofbourov.⁵ Methods have also been devised employing but one beam of light, so that instead of matching intensities on a photographic plate, the energy of the beam is measured by a thermopile or, more usually, a photoelectric cell and accessory apparatus, with the absorption cell in the beam and without it. Among photoelectric spectrophotometric methods are those of Hogness, Zscheile and Sidwell.⁶ Automatic recording devices have also been constructed. A continuous representation of the absorption curve of a rapidly changing system can be obtained by the aid of a cathode-ray oscillograph, according to Holiday and Smith.⁷ The fine structure of the absorption spectra of gases is obtained by micrometric tracings of photographed spectra.⁸

In the absorption curve of a substance there is plotted against wave-lengths as abscissae the ratio of the light passing through the absorbing substance (I_x) to that incident upon it (I_0). This ratio is given by the logarithmic relation $I_x/I_0 = e^{-kcd}$, in which c is the concentration of a solution (or pressure of a gas), d the thickness of the absorbing layer and k is a constant characterizing the absorption of the substance at the wave-length in question. A plot of k against the wave-lengths gives graphically the absorption of the substance throughout the spectral range investigated. k is known as the absorption coefficient, and varies with the wave-length. The numerical value of k is obtained by dividing the product cd into the natural logarithm of the ratio of I_0/I_x . In practice, most workers employ the more convenient common logarithms. The terms "extinction coefficient" and "absorption coefficient" are rather indiscriminately employed to designate the values obtained by the use of either logarithmic base. In general, German authors follow Kayser in using the term "absorption coefficient" for values based on natural logarithms and English workers follow Bunsen and Roscoe in using "extinction coefficient" for values based on the use of logarithms to the base ten. The distinction in terms is by no means universally observed.

³ See Ley, H., and Volbert, F., *Z. wiss. Phot.*, 23, 41 (1924).

⁴ de Lazlo, H., *J. Phys. Chem.*, 32, 505 (1928).

⁵ Loofbourov, J. R., *Bull. Basic Sci. Research*, 5, 46 (1933).

⁶ Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr., *J. Phys. Chem.*, 41, 379 (1937).

⁷ Holiday, E. R., and Smith, F., *Nature*, 134, 102 (1934).

⁸ See Harrington, E. A., *J. Opt. Soc. Am.*, 16, 211 (1928); Gull, H. C., and Martin, A. E., *J. Sci. Instruments*, 12, 379 (1935).

The following bibliography includes but a few of the more important papers on the measurement of absorption spectra and their applications to the study of constitution. A considerable proportion of them, indicated separately, are concerned primarily with the limitations of the photographic method because of the failure of the relation between the intensity of the light and the blackening of the plate. van Halban, H., and Eisenbrand, J., *Proc. Roy. Soc.*, 116A, 153 (1927); *Z. wiss. Phot.*, 25, 138 (1928). Baly, E. C. C., and Riding, R. W., *Proc. Roy. Soc.*, 113A, 709 (1927). Schaum, K., and Kellner, H. M., *Z. wiss. Phot.*, 24, 85 (1926). Fromherz, H., *Z. physik. Chem.*, 1B, 301 (1928). Gage, F. H., *J. Sci. Instruments*, 6, 256 (1929). Conrad-Billroth, H., *Z. physik. Chem.*, 14B, 122 (1931). Schlessinger, M., *Biochem. Z.*, 235, 70 (1931). Ley, F., and Volbert, F., *Z. physik. Chem.*, 130, 308 (1927). Twyman, F., *Proc. Phys. Soc. (London)*, 45, 1 (1933). Ginsel, L. A., *Physica*, 3, 578 (1936). von Halban, H., Kortüm, G., and Szigetti, B., *Z. Elektrochem.*, 42, 628 (1936). Miller, E. S., *Plant Physiol.*, 12, 667 (1937). Albers, V. M., and Knorr, H. V., *J. Opt. Soc. Am.*, 23, 121 (1938). Deck, W., *Helv. Phys. Acta*, 11, 1 (1937). Schlaer, S., *J. Opt. Soc. Am.*, 28, 18 (1938). P. J. Kippen Zonen, *J. Sci. Instruments*, 15, 141 (1938). Papers dealing with the limitations of the reciprocity law and the Schwarzschild law in photographic materials: Harrison, G. R., *J. Opt. Soc. Am.*, 11, 341 (1925); 19, 267 (1929). Kellner, H. M., *Z. wiss. Phot.*, 24, 41, 79 (1926). Dorgelo, H. B., *Physik. Z.*, 26, 756 (1925). Fabry, C., *Phot. J.*, 66, 328 (1926). Jones, L. A., and Hall, V. C., *J. Opt. Soc. Am.*, 13, 443 (1926). Wehby, J. H., *J. Opt. Soc. Am.*, 23, 316 (1933). Mees, C. E. K., *J. Opt. Soc. Am.*, 23, 229 (1933). Harvey, A., *Science Progress*, 27, 650 (1933). Kinele, H., *Naturwiss.*, 23, 762 (1935). Pestemer, M., and Schmidt, G., *Monatsh.*, 69, 399 (1936). Lambrey, M., and Corbière, J., *Compt. rend.*, 201, 1351 (1935). van Kreveld, A., and Ornstein, L. S., *Proc. Acad. Sci. Amsterdam*, 39, 478 (1936). de Langhe, J. E., *Physica*, 3, 904 (1936). Kiss, A., and Gerendás, M., *Acta Lit. Sci. Regiae Univ. Hung. Francisco-Josephinae, Sect. Chem. Mineral. Phys.*, 5, 153 (1937); *Chem. Abs.*, 32, 1577 (1938).

THE FORMATION AND DECOMPOSITION OF THE HYDROGEN HALIDES

The Decomposition of Hydrogen Iodide. According to Rollefson and Booher,⁹ the first mention of this reaction was by Lemoine.¹⁰ Also, the reaction was early studied by Bodenstein.¹¹ Warburg¹² found a quantum yield of approximately two for the wave-lengths 2070, 2530 and 2820Å. In Chapter 12 it was shown that this observation could be accounted for equally well by either the mechanism of primary dissociation proposed by Warburg or of primary excitation of the hydrogen iodide molecule proposed by Stern and Volmer. Attempts to decide between the two by Bodenstein on the basis of kinetic measurements under varied experimental conditions, especially in the presence of foreign gases, were inconclusive. The data which eventually showed the correctness of the Warburg mechanism were predominantly physical and, as discussed in Chapter 14, came from the finding that the absorption spectrum of hydrogen iodide is continuous. At this point, we may consider in more detail the spectroscopic evidence regarding the absorption not only of hydrogen iodide but also of the products of the reaction, hydrogen and iodine.

Tingey and Gerke¹³ found the absorption of hydrogen iodide to be entirely continuous and to begin at 3320Å, corresponding to 86 kcal.; Coehn and Stuckardt¹⁴ had previously placed this value at 3340Å. It has been generally assumed¹⁵ that the iodine atom produced in the dissociation is excited as in the case of the halogen from hydrogen chloride and hydrogen bromide. The energy of excitation of iodine is, from its atomic spectrum, 21.5 kcal. This, when subtracted from the energy corresponding to the long-wave threshold of the absorption spectrum 86 kcal. leaves 64.5 kcal., in fair agreement with the heat of dissociation of HI into normal atoms, 69 kcal. Goodeve and Taylor¹⁶ calculated a potential energy curve for the upper state from the eigenfunction of the ground state and their own observations of the extinction values. Rollefson and Booher¹⁷ found the absorption to extend as far as 3900Å at least, and gave evidence that at 4120Å, dissociation into normal atoms can occur; at 3120Å, the iodine atom may be excited. Datta¹⁸ places the absorption limit at 4040Å.

Hydrogen. The fact that hydrogen absorbs only in the extreme ultraviolet range eliminates this substance as an absorbing component which might affect either the dissociation of hydrogen iodide or the combination of hydrogen and iodine. Dieke and Hopfield¹⁹ found that in a 100 cm. layer at pressures of 2 to 50 mm. of mercury, hydrogen does not absorb wave-lengths longer than 1115Å. Below this, it exhibits two band systems, the members of both of which converge at 849.4Å to a region of continuous absorption corresponding to dissociation into a normal and an excited atom.

Iodine. Observations by Dymond²⁰ of the short wave-length limit of fluores-

⁹ Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).

¹⁰ Lemoine, G., *Ann. Chim. Phys.*, **12**, 145 (1877).

¹¹ Bodenstein, M., *Z. physik. Chem.*, **22**, 23 (1897); **85**, 329 (1913); Bodenstein, M., and Lieneweg, F., *Z. physik. Chem.*, **119**, 123 (1926).

¹² Warburg, E., *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

¹³ Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926); see also Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926); Lewis, B., *Nature*, **119**, 493 (1927).

¹⁴ Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916).

¹⁵ Lewis, B., *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).

¹⁶ Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **154A**, 181 (1936).

¹⁷ Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).

¹⁸ Datta, A. K., *Z. Physik*, **77**, 404 (1932).

¹⁹ Dieke, G. H., and Hopfield, J. J., *Phys. Rev.*, **30**, 400 (1927); *Z. Physik*, **40**, 299 (1926).

²⁰ Dymond, E. G., *Z. Physik*, **34**, 553 (1925).

cence were important in establishing the generally accepted interpretation of continuous spectra as indicative of dissociation. Iodine vapor exhibits bands which converge at 4989Å to a continuous absorption region.²¹ Fluorescence can be induced by wave-lengths longer than the convergence limit but cannot be observed in iodine vapor irradiated by wave-lengths within the continuous region. The dissociation produces a normal and an excited iodine atom.²²

Extinction values have been given by Vogt and Königsberger²³ and, more recently, by Rabinowitsch and Wood.²⁴ The effect of varying the pressure of the iodine vapor has been studied by Perot and Collinet,²⁵ and the influence of foreign gases on the color of iodine vapor reported by Wright and McGregor.²⁶ The extinction coefficients drop off toward shorter wave-lengths in the continuous region. In the region below 2763Å, iodine vapor exhibits a new region of banded absorption, the interpretation of which is not yet clear.²⁷

By spectroscopic methods, Rabinowitsch and Wood²⁸ measured the quantum yield of the dissociation of iodine in the presence of foreign gases in three spectral regions. If the yield is unity in the continuum, it is 1.14 in the band region immediately on the long-wave side, and 1.10 at a point in the band region further from the limit. This indicates that all excited molecules dissociate by collisions with foreign molecules. Therefore, the quenching of the fluorescence is not due to the process $I_2^* + X \rightarrow I_2 + X$, but rather to $I_2^* + X \rightarrow I + I + X$. Quenching usually occurs at the first collision of an excited molecule with a foreign molecule, except in the case of helium which requires ten or more collisions before dissociation results. The atoms recombine mainly at the walls at low pressures. Under these conditions dissociation increases with the pressure. At higher pressures, however, the recombination occurs as a homogeneous reaction in the gas phase. The transition occurs sharply at 250 mm. in helium and 40 mm. in carbon dioxide. The dissociation is then proportional to the square root of the light intensity and to the inverse square root of the pressure, in accordance with the theoretical expression for recombination by three-body collisions. One double collision in 530 is a recombining one in helium and one in 50 in carbon dioxide at atmospheric pressure. The efficiency of the third body increases with its molecular size and with the intensity of the molecular fields of the colliding particles.

To decide between the mechanisms proposed (Chapter 12) for the decomposition of hydrogen iodide, Bonhoeffer and Farkas²⁹ studied the reaction at low pressures at which, were the reaction due to excited molecules, some re-radiation of the energy of excitation would be expected since the period between deactivating collisions would be longer than the life of the excited state. Since they could detect no fluorescence, it was concluded that the mechanism of Warburg (dissociation) must apply. Furthermore, exposure to light resulted in a fall of pressure

²¹ Mecke, R., *Ann. Physik*, **71**, 104 (1923); Brown, W. G., *Phys. Rev.*, **38**, 709 (1931).

²² Turner, L. A., *Phys. Rev.*, **21**, 397 (1926).

²³ Vogt, K., and Königsberger, J., *Z. Physik*, **13**, 292 (1923).

²⁴ Rabinowitsch, E., and Wood, W. C., *Trans. Faraday Soc.*, **32**, 540 (1936).

²⁵ Perot, A., and Collinet, M., *Compt. rend.*, **180**, 2030 (1925).

²⁶ Wright, R., and McGregor, T., *J. Chem. Soc.*, 1364 (1929).

²⁷ Pringsheim, P., and Rosen, B., *Z. Physik*, **50**, 1 (1928); Sponer, H., and Watson, W., *Ibid.*, **56**, 184 (1929); Kimura, M., and Miyazaki, M., *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **10**, 33 (1929). Further recent data on the absorption of iodine, particularly in the long-wave regions, have been given by Hirschlauff, E., *Z. Physik*, **75**, 315 (1932); Agarbiceanu, T., *Compt. rend.*, **194**, 702 (1932); Kondratjev, V., and Polak, L., *Physik. Z. Sowjetunion*, **4**, 764 (1933); Skorko, E., *Acta Phys. Polonica*, **3**, 191 (1934); Warren, D., *Phys. Rev.*, **47**, 1 (1935). The Budde effect differs from that of the other halogens in being proportional to the light intensity rather than to its 0.5 power. Narayana, T. S., *Indian J. Physics*, **9**, 111, 117 (1934); *Chem. Abs.*, **29**, 2847 (1935).

²⁸ Rabinowitsch, E., and Wood, W. C., *J. Chem. Physics*, **4**, 358, 497 (1936).

²⁹ Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

which could be attributed only to the adsorption of free iodine atoms on the walls of the vessels. The same fall in pressure was also observed during the irradiation of hydrogen bromide.

Wave-lengths between 3000 and 2200Å cause the complete decomposition of hydrogen iodide.³⁰ The velocity is independent of temperatures below 120°C.; it is lowered by addition of either iodine vapor or of an excess of hydrogen. At the beginning of reaction, the velocity remains constant for a time, then falls to that of a unimolecular reaction, and later falls again. The falling off in the rate toward the end of the decomposition is hastened when the initial pressure of hydrogen iodide is high and the temperature low. The initial reaction velocity appeared to increase approximately in proportion to the initial concentration of hydrogen iodide. Quantum yields somewhat higher than those of Warburg have been reported by Lewis,³¹ his values being 2.36 for the 2080Å and 2.35 for the 2530Å zinc lines. The product of the intermediate reaction $H + HI \rightarrow H_2 + I$ is 25 per cent para-hydrogen at room temperatures. At 170°Abs. the hydrogen produced contains 2 per cent more para-hydrogen than does normal hydrogen.

Studies of the photochemical combination of hydrogen and iodine have been made by Coehn and Stuckardt,³² who found that reaction can occur only in the ultraviolet region, and by Sasaki and Nakamura.³³ The latter workers found no combination could be induced by radiations longer than 3100Å. It is suggested that hydrogen atoms may be produced by collisions of the second kind between hydrogen molecules and iodine molecules excited by the absorption of the 1800Å line, although dissociation of iodine might be expected. The production of hydrogen atoms is essential that the reaction may go at ordinary temperatures since the reaction $I + H_2 \rightarrow HI + H$ is too endothermic to proceed. There is some evidence that the photocombination occurs under the influence of visible light at temperatures of 430-466°C.³⁴

Other Halogen Hydrides.³⁵ Berthelot and Gaudechon³⁶ found that, as in the case of thermal decompositions, the stabilities of the hydrogen halides in light decrease with increasing atomic weights of the halogens. Those substances which require high temperatures for thermal decomposition require the shortest wave-lengths in the ultraviolet. For the decomposition of hydrogen chloride, wave-lengths shorter than 2000Å are required to produce even a slow decomposition. Under similar conditions, hydrogen bromide is rapidly and completely decomposed. Coehn and Stuckardt³⁷ effected reactions of hydrogen halides from both

Table 19.—Photostationary States of Hydrogen Halides.

Acid	In quartz (2200Å)	In Uviol glass (2500Å)	In Jena glass (3000Å)?
Hydriodic	92.2	100	100
Hydrobromic	100	about 20	0
Hydrochloric	0.42	0	0.

³⁰ Trautz, M., and Scheifele, B., *Z. wiss. Phot.*, **24**, 177 (1926).

³¹ Lewis, B., *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).

³² Coehn, A., and Stuckardt, K., *Z. physikal. Chem.*, **91**, 722 (1916).

³³ Sasaki, N., and Nakamura, K., *Anniversary Volume Dedicated to M. Chikashige (Kyoto Imp. Univ.)* 299 (1930); *Chem. Abs.*, **25**, 2921 (1931).

³⁴ Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926).

³⁵ Almost no work has been reported on the combination of hydrogen and fluorine. See, however, Bodenstein, M., and Jockersch, H., *Z. anorg. Chem.*, **231**, 24 (1937).

³⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913); *J. Chem. Soc.*, **104** (II), 369 (1913).

³⁷ Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916); *Chem. Abs.*, **11**, 749 (1917).

sides of the equilibrium in vessels of quartz, Uviol glass and Jena glass. These glasses roughly delimited three spectral ranges. The percentage decomposition of each acid at equilibrium is listed in Table 19.

The reactions of hydrogen bromide are very well adapted for the presentation of the method devised by Bodenstein for the treatment of the kinetics of photochemical reactions in general and will be discussed in detail as representative of the methods employed in studying photochemical mechanisms. The case of hydrogen chloride is so complicated that a separate chapter is devoted to its consideration. Before proceeding to a consideration of kinetics, the essential data on the absorption spectra of bromine vapor and hydrogen bromide will be presented.

Absorption of Bromine. In the visible range there is absorption from about 6000Å to 3500Å, the maximum occurring at about 4100Å.³⁸ Bands from about 5700Å converge to a limit at 5107Å.³⁹ At shorter wave-lengths the absorption is continuous, implying a dissociation into a normal atom and one in a metastable state with excitation energy of 10.5 kcal.⁴⁰ In the ultraviolet region, bromine vapor at higher pressures exhibits a continuous region from 2700Å to the limit of observations at 1560Å.⁴¹ Brown⁴² has found another band region between 7500 and 6400Å, the bands of which apparently converge to a limit indicative of dissociation into two normal atoms. (A dissociation energy of 45.2 kcal. corresponds to 6290Å.) Other absorption studies were made by Barratt and Stein,⁴³ Nakamura,⁴⁴ and Hays.⁴⁵ The excitation of fluorescence within the range 5000-5600Å has been studied by Daure.⁴⁶ Wave-lengths in the continuous band below 5000Å excite no fluorescence.

Absorption by Hydrogen Bromide. Hydrogen bromide absorbs continuously in the shorter ultraviolet.⁴⁷ Tingey and Gerke⁴⁸ found continuous absorption to begin at a wave-length which varies with the mass of gas studied, approaching 2640Å as a limit as the mass of gas is increased. Coehn and Stuckardt had given 2650Å. The absorption limit was unaffected by temperature over the range 25° to 400°C. Datta, however, placed the long-wave threshold at 3260Å. The formation of free atoms has been established by Bonhoeffer and Farkas.⁴⁹ Goodeve and Taylor⁵⁰ believe the molecule dissociates into atoms in normal states. Trivedi's spectroscopic value for the dissociation energy is 92 kcal.⁵¹ There have been but few studies of the decomposition of hydrogen bromide but the work of Warburg⁵² is so conclusive that it is generally accepted that the primary process, as in the case of hydrogen iodide is one of photodissociation. The quantum yield is 2.08 at 2070Å and 2.00 at 2530Å.

Combination of Hydrogen and Bromine. At ordinary temperatures, this

³⁸ Bovis, P., *J. Phys. Radium*, **10**, 267 (1929); Kuhn, H., *Z. Physik*, **39**, 77 (1926).

³⁹ Brown, W. G., *Phys. Rev.*, **38**, 1179 (1931).

⁴⁰ Turner, L. A., *Phys. Rev.*, **21**, 397 (1926).

⁴¹ Cordes, H., and Sponer, H., *Z. Physik*, **63**, 334 (1930).

⁴² Brown, W. G., *Phys. Rev.*, **39**, 777 (1932). For the absorption of liquid bromine, see Porret, D., *Proc. Roy. Soc.*, **A162**, 414 (1937).

⁴³ Barratt, S., and Stein, C. P., *Proc. Roy. Soc.*, **122**, 582 (1929).

⁴⁴ Nakamura, G., *Mem. Coll. Sci. Kyoto*, **9**, 335 (1926); *Chem. Abs.*, **21**, 2431 (1927).

⁴⁵ Hays, M. B., *J. Frank. Inst.*, **208**, 363 (1929).

⁴⁶ Daure, P., *Compt. rend.*, **183**, 31 (1926).

⁴⁷ Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 737 (1916); Warburg, E., *Berlin Akad. Ber.*, **314** (1916); 300 (1918); Datta, A. K., *Z. Physik*, **77**, 404 (1932).

⁴⁸ Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1844 (1926).

⁴⁹ Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

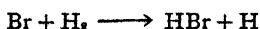
⁵⁰ Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **A152**, 221 (1935).

⁵¹ Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 29 (1936); *Chem. Abs.*, **30**, 4760 (1936).

⁵² Warburg, E., *Berlin Akad. Ber.*, **314** (1916); 300 (1918).

reaction occurs to but a very slight extent, Pusch⁵³ finding that the absorption of a thousand quanta produces only one molecule of hydrogen bromide. At temperatures of 100° to 200°C., Kastle and Beatty⁵⁴ found a reaction to occur. At still higher temperatures (200-300°C.) a thermal reaction occurs in the dark. The kinetics of the dark reaction have been studied by Bodenstein and Lind.⁵⁵ Interpretation of this reaction given by Christiansen,⁵⁶ Polanyi⁵⁷ and Herzfeld⁵⁸ involved the thermal dissociation of bromine into atoms.⁵⁹

From the absorption data, it is evident that the photoreaction also proceeds by a mechanism involving free bromine atoms. That the quantum yield exceeds two only at high pressures of hydrogen and that the hydrogen-bromine mixture is insensitive to light at ordinary temperatures are explained on the basis that the reaction



is endothermic. The necessary activation energy can be supplied only thermally at high temperatures.⁶⁰

Bodenstein and Lütke Meyer⁶¹ studied the reaction rate spectrophotometrically by measuring the disappearance of the bromine. They employed temperatures of 160-218°, and irradiated the mixture with moderately intense light from a tungsten arc. The combination takes place with a velocity about 300 times as great as that of the dark reaction at the same temperature. They found also that, under conditions of weak absorption and at the beginning of the reaction, the rate of formation of hydrogen bromide was proportional to the concentration of hydrogen and to the square root of the bromine concentration and the square root of the absorbed energy. When absorption is complete, and in later stages of the reaction when a stationary concentration of bromine atoms has been reached, the rate of the reaction is expressed by

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2(\text{H}_2) \sqrt{\frac{\text{No. of quanta absorbed}}{k_3}}}{1 + \frac{k_4(\text{HBr})}{k_3(\text{Br}_2)}}$$

The various k values employed refer to the rate constants in the numbered equations which can be set down for the primary process and for the reactions of the products of this reaction with all other substances present. In this case these reactions are

1. $\text{Br}_2 + h\nu \longrightarrow 2\text{Br}$
2. $\text{Br} + \text{H}_2 \longrightarrow \text{HBr} + \text{H} - 16.2 \text{ kcal.}$
3. $\text{H} + \text{Br}_2 \longrightarrow \text{HBr} + \text{Br} + 40.5$
4. $\text{H} + \text{HBr} \longrightarrow \text{H}_2 + \text{Br} + 16.2$
5. $\text{Br} + \text{Br} \longrightarrow \text{Br}_2 + 45.2$

⁵³ Pusch, L., *Z. Elektrochem.*, **24**, 336 (1918).

⁵⁴ Kastle, J. H., and Beatty, W. A., *Am. Chem. J.*, **20**, 159 (1898).

⁵⁵ Bodenstein, M., and Lind, S. C., *Z. physik. Chem.*, **57**, 168 (1906).

⁵⁶ Christiansen, J. A., *Kgl. Danske Videnskab Selskab, Math.-fys. Medd.*, **1**, 14 (1919); *Chem. Abs.*, **14**, 1085 (1920).

⁵⁷ Polanyi, M., *Z. Elektrochem.*, **26**, 50 (1920).

⁵⁸ Herzfeld, K. F., *Z. Elektrochem.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919).

⁵⁹ See, however, Skrabal, A., *Ann. Physik*, **82**, 138 (1927).

⁶⁰ Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926). Compare the analogous chlorine reactions in the next chapter.

⁶¹ Bodenstein, M., and Lütke Meyer, H., *Z. physik. Chem.*, **114**, 208 (1924).

The plausibility of each of the secondary reactions is then considered. Exothermic reactions are always admitted, although in the case of certain recombinations of free atoms the reaction is not possible except as a result of three-body collisions involving a foreign inert gas or a wall reaction. Endothermic reactions are excluded or admitted, depending upon the possibility of securing the necessary activation energy thermally in a reasonable fraction of collisions at the temperature of the reactants.

The intermediate products are considered to exist (except at the beginning of the irradiation period) in stationary concentrations, reactions leading to their removal summing up to a removal rate equal to the sum of the rates of the reactions by which they are formed. Thus, in this case,

$$\begin{aligned}\frac{d(\text{Br})}{dt} &= 2k_1(\text{Br}_2) + k_3(\text{H})(\text{Br}_2) + k_4(\text{H})(\text{HBr}) \\ &\quad - \frac{d(\text{Br})}{dt} = k_2(\text{Br})(\text{H}_2) + 2k_5(\text{Br}^2)\end{aligned}$$

Similarly, for the stationary concentration of H atoms,

$$k_3(\text{H})(\text{Br}_2) = k_4(\text{H})(\text{HBr}) + k_2(\text{Br})(\text{H}_2).$$

Solution of these simultaneous equations makes it possible to express the stationary concentrations of the bromine atoms and of hydrogen atoms in terms of rate constants and the concentrations of hydrogen, bromine and hydrogen bromide molecules. Thus, by subtracting the second from the first equation and solving for (Br) , the value $k_1/k_5 (\text{Br}_2)$ is obtained. Solving the second equation alone gives for the hydrogen atom concentration

$$\frac{k_2(\text{Br})(\text{H}_2)}{k_3(\text{Br}_2) + k_4(\text{HBr})}$$

and by substituting in this the value just found for the bromine atom concentration, the stationary H atom concentration becomes

$$[\text{H}] = \frac{k_2(\text{H}_2) \sqrt{\frac{k_1}{k_5} (\text{Br}_2)}}{k_3(\text{Br}_2) + k_4(\text{HBr})}$$

The secondary reactions leading to the formation of hydrogen bromide are next summed up and those leading to its destruction deducted.

$$\frac{d(\text{HBr})}{dt} = k_2(\text{Br})(\text{H}_2) + k_3(\text{H})(\text{Br}_2) - k_4(\text{H})(\text{HBr})$$

By substituting the calculated values for the stationary states of hydrogen and bromine atoms and simplifying algebraically, it is then possible to arrive at an equation which will express the overall kinetics of the reaction. In this case the equation is

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2(\text{H}_2) \sqrt{\frac{k_1}{k_5} (\text{Br}_2)}}{1 + \frac{k_4(\text{HBr})}{k_3(\text{Br}_2)}}$$

In deriving this expression the formation of bromine atoms was assumed to occur thermally. When formation occurs by the absorption of light as in equation (1),

the stationary concentration of bromine atoms is given by $(\text{Br}) = \sqrt{\frac{n}{k_5}}$, in which n

is the number of quanta absorbed per second. In the final equation the radical $\sqrt{\frac{k_1}{k_5}}(\text{Br}_2)$ must be replaced by $\sqrt{\frac{n}{k_5}}$. The final result agrees with the observations

of Bodenstein and Lütkemeyer that the rate is proportional to the square root of the light intensity at complete absorption. In this expression, it is implied that at the start of the reaction, before hydrogen bromide has formed to an appreciable extent, the denominator becomes unity and the rate is proportional to the hydrogen concentration and the square root of the light intensity. This was observed. Furthermore, if not all of the light is absorbed, the rate also is proportional to the square root of the concentration of the absorbing component, bromine. This also was observed. An examination of the derivation of the rate equation reveals why it is that in reactions involving the dissociation of a molecule by light, the square root of the intensity (or of the absorbing component concentration) so frequently enters the rate expression. It may be noted that in the case of this reaction the derivation was made on the basis of a mechanism for the dark reaction, which was found to give agreement with the expression for the kinetic data of Bodenstein and Lind for the thermal reaction;⁶² the necessary modification to make the equation express the photochemical reaction was made subsequently by Bodenstein and Lütkemeyer. The effect of hydrogen bromide in retarding the reaction, as indicated in the denominator, is due to its ability to remove hydrogen atoms by reaction (4). The greater speed of the photochemical reaction is due to the greater stationary concentration of bromine atoms produced by light as compared to those produced thermally at the same temperature (in the range studied). The temperature coefficient of the photoreaction was found to be 1.5 and that of the dark reaction 2.0. From the similarity of mechanisms it was found possible to calculate either temperature coefficient from the other. The value of this coefficient for the photoreaction is due to reaction (3); the temperature coefficient of the dark reaction involves also the thermal dissociation of bromine molecules. The value of 1.5 for the light reaction indicated an activation energy of 17.6 kcal.

The second term in the denominator of either the photo- or thermal reaction rate equation involves a ratio of k_4/k_3 . In the thermal reaction this is about 1/10 and independent of temperature. Bodenstein and Jung⁶³ found the ratio 1/8.4 for experiments both in strong light at room temperature and at 302° in darkness. This independence of the ratio over a wide temperature range indicated that reactions (3) and (4) require no activation energy. The heat of a reaction is the difference between the activation energies of the forward and reverse reactions. As (4) is the reverse of (2) and as (4) has a zero activation energy, the activation energy found for (2) from the temperature coefficient of the light reaction must also be the heat of reaction (2). Using this value, Bodenstein and Jung combined it with the heats of certain other known reactions in order to calculate a value for the heat of dissociation of hydrogen of 107 kcal. This has subsequently

⁶² Bodenstein, M., and Lind, S. C., *Z. physik. Chem.*, **57**, 168 (1906).

⁶³ Bodenstein, M., and Jung, G., *Z. physik. Chem.*, **121**, 127 (1926).

been corrected by the use of a better value for one of the reactions they use, to give 103.6 kcal, which is in good agreement with the spectroscopic value 101.9 kcal.

Still other information was derived by Bodenstein and Lütkemeyer from their data. Division of the photo rate equation by the dark rate equation gives for the quotient of the observed rates

$$\frac{I_0}{k_6} \bigg/ \frac{k_1(\text{Br}_2)}{k_5}$$

The ratio k_1/k_5 was known from the work of Bodenstein and Cramer⁶⁴ on the thermal equilibrium constant for the dissociation of bromine. It was therefore possible to calculate k_6 . They found in this way that only about one in 800 of the collisions between bromine atoms leads to the formation of molecules. Furthermore this figure appeared to be independent of the temperature and total pressure. Briers and Chapman⁶⁵ calculated the mean life of the bromine atoms to be 0.063 second. That the removal rate of bromine atoms should be independent of pressure was unexpected in view of the necessity of three-body collisions for recombination and led Jost and Jung⁶⁶ to a study of the effect of variation of total pressure over a wide range on the concentration of bromine atoms and therefore also upon the rate of the reaction. The result was the finding that the reaction velocity is inversely proportional to the square root of the total pressure. An explanation of the apparent discrepancy between these results and those of Bodenstein and Lütkemeyer was given by Bodenstein, Jost and Jung.⁶⁷ They pointed out that at low pressures the effects of diffusion of the bromine atoms to the walls where recombination could occur had to be taken into account. At low pressures and weak light intensities (*i.e.*, low concentration of bromine atoms) the rate of formation of hydrogen bromide was found to be proportional to the light intensity rather than to its square root. Jost⁶⁸ also found that the formation of hydrogen bromide can be brought about by light of wave-lengths greater than 5107 Å. and therefore in the banded region of the absorption spectrum of bromine. Here the excited bromine molecules yield bromine atoms on collision with other molecules. The bromine atoms recombine in triple collisions and may also be destroyed on the walls, so that the latter have a characteristic effect on the reaction velocity. The activated bromine atoms formed in the primary reaction affect the reaction velocity in the same manner as unactivated ones because they suffer deactivation before they can react. The velocity constants of the single reactions involved in the formation of hydrogen bromide were recalculated from these data and found in agreement with theory.

Ritchie⁶⁹ studied the effect of inert gases on the removal of bromine atoms as affecting the rate of the hydrogen bromide formation at 200°C., the results applying either to the thermal or the light reaction. Under conditions favoring the removal of the atoms to the wall, acceleration of the reaction was produced by foreign gases in the order $\text{CCl}_4 > \text{CO}_2 > \text{N}_2$ and $\text{O}_2 > \text{A} > \text{H}_2$ and He. When the removal was primarily by triple collisions in the gas phase, the efficiency was in the order $\text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{A} > \text{He} > \text{H}_2$. Rabinowitsch and Lehmann⁷⁰ find

⁶⁴ Bodenstein, M., and Cramer, F., *Z. Elektrochem.*, **22**, 327 (1916).

⁶⁵ Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).

⁶⁶ Jost, W., and Jung, G., *Z. physik. Chem.*, **3B**, 83 (1929).

⁶⁷ Bodenstein, M., Jost, W., and Jung, G., *J. Chem. Soc.*, 1153 (1929).

⁶⁸ Jost, W., *Z. physik. Chem.*, **134**, 92 (1928).

⁶⁹ Ritchie, M., *Proc. Roy. Soc.*, **146A**, 828 (1934); Hilferding, K., and Steiner, W., *Z. physik. Chem.*, **B30**, 399 (1935).

⁷⁰ Rabinowitsch, E., and Lehmann, H. I., *Trans. Faraday Soc.*, **31**, 689 (1935).

the velocity of homogeneous recombination in the presence of helium to vary inversely with the square root of pressure in accordance with the three-body mechanism, and not according to a conceivable mechanism involving the bromine molecule. At atmospheric pressure, about one double collision in 1300 leads to recombination; this is of the order of the total number of triple collisions expected. Argon and nitrogen are more effective than helium in promoting recombination of bromine atoms.⁷¹

Armour and Ludlam⁷² state that in a streaming mixture of hydrogen and bromine vapor irradiated by the 1850A line of an aluminum spark less than 1 per cent (by weight) of the bromine enters into combination. This was unaltered by a ten-fold variation of the intensity.

It may be noted that Lewis and Rideal believed the reaction to be inhibited by extreme drying. Bodenstein and Jost⁷³ however, consider this to be unproved; they attribute the results to possible reaction between the hydrogen bromide and the drying agent employed.

The reaction of hydrogen and bromine has been discussed in considerable detail to show the applicability of the concept of stationary states to the formulation⁷⁴ of rate expressions from assumed mechanisms and also to illustrate the manner in which photochemical data may be employed as aids to the solution of other physical chemical problems, as for example, the heat of dissociation of hydrogen or the rates of recombination of bromine atoms. In this way the manner in which photochemical investigations interlock with other phases of physical chemistry becomes apparent.

REACTIONS OF INTERHALOGEN COMPOUNDS

Mellor and Iredale⁷⁵ find hydrogen and iodine chloride to react rapidly in strong light if the hydrogen pressure is large compared with that of the iodine chloride, indicating that this condition favors the reaction $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$ so that excited chlorine atoms may not be required for reaction. In thin glass bulbs a reaction between hydrogen and iodine chloride occurs very slowly in artificial light, more rapidly in diffuse daylight and very rapidly in direct sunlight. The products are chiefly iodine and hydrogen chloride. They later state that the reaction can be brought about with pressures of hydrogen comparable with that of the iodine chloride.⁷⁶ Methane also reacts rapidly with iodine chloride in light.⁷⁷

⁷¹ See also Urmston, J., and Badger, R. M., *J. Am. Chem. Soc.*, **56**, 343 (1934).

⁷² Armour, R. W., and Ludlam, E. B., *Proc. Roy. Soc. Edinburgh*, **49**, 91 (1929), *Chem. Abs.*, **23**, 3856 (1929).

⁷³ Bodenstein, M., and Jost, W., *J. Am. Chem. Soc.*, **49**, 1416 (1927).

⁷⁴ For a discussion of the validity of the method, see Bodenstein, M., *Trans. Faraday Soc.*, **27**, 409 (1931).

⁷⁵ Mellor, D. P., and Iredale, T., *Nature*, **127**, 93 (1931).

⁷⁶ Cf. Rollefson, G. K., and Lindquist, F. E., *J. Am. Chem. Soc.*, **53**, 1184 (1931).

⁷⁷ Ashley, S., and West, W., *Nature*, **127**, 308 (1931).

Chapter 18

The Hydrogen-Chlorine Combination

Although apparently one of the simplest photochemical changes, this reaction has been for over a century the subject of an extraordinary amount of investigation because actually it has offered extreme difficulties in both experimental observation and in interpretation. The experimental results have frequently been in disagreement, largely because small quantities of impurities exert such a remarkable effect upon the reaction that reproducible results are difficult to secure. Oxygen, which can be removed from chlorine only with great difficulty, has an inhibiting effect, difficult to eliminate. Other impurities, entirely unsuspected, have been responsible for an inert period after the start of illumination before the reaction begins to build up to its maximum rate. Since studies on this reaction were among the first quantitative photochemical investigations, the finding of this induction period was for a time assumed to be a general photochemical phenomenon, an error which greatly affected the early development of photochemical theory. A thorough review of the history of this reaction would fill many pages. Since excellent summaries are available¹ and since most of the data are concerned with the effects of visible rather than ultraviolet light, the account in this chapter will be limited to a consideration of certain of the more significant features of the work on the reaction, following a statement of the viewpoint at present most generally held in regard to the mechanism.

SPECTRAL ABSORPTION DATA

1. **Hydrogen Chloride.** The absorption of hydrogen chloride consists only of four continuous bands in the short-wave region (2150-1850, 1750-1650, 1580-1290 and 1270-1240Å). The absorption spectra of the halide apparently has no significance for the course of the reaction involving hydrogen and chlorine.² When irradiated in its absorption region, hydrogen chloride dissociates into a normal hydrogen and an excited chlorine atom, Trivedi³ finding from the absorption spectrum a heat of dissociation equivalent to 103.9 kcal. Coehn and Wassiljewa⁴ and Berthelot and Gaudechon⁵ observed slight decomposition to occur as a result of irradiating hydrogen chloride in this wave-length region. According to Schultz⁶ not more than 5 molecules may be decomposed per quantum absorbed.

2. **Absorption of Chlorine.** Chlorine absorbs in two broad regions. The first, to which the gas owes its color, extends from about 6430Å (or possibly

¹ Griffith, R. O., and McKeown, A., "Photo-Processes in Gaseous and Liquid Systems," London, Longmans, Green and Co., 1929, Chapter X; Bodenstein, M., *Trans. Faraday Soc.*, **27**, 413 (1931); Thon, N., *Fortschritt Chem. Physik, physik. Chem.*, **18**, No. 11 (1926); Marshall, A. L., *Trans. Am. Electrochem. Soc.*, **49**, 143 (1926).

² Leifson, S., *Astrophys. J.*, **63**, 73 (1926).

³ Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 18 (1936); *Chem. Abs.*, **30**, 4759 (1936).

⁴ Coehn, A., and Wassiljewa, A., *Ber.*, **42**, 3183 (1909).

⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913).

⁶ Schultz, C. T., *J. chim. phys.*, **26**, 506 (1929); *Brit. Chem. Abs. A*, 173 (1930).

longer) to about 2500Å. Its maximum lies at about 3340Å. Extinction values have been given by v. Halban and Siedentopf.⁷ There is a minimum in the yellow and the absorption then increases toward longer wave-lengths to a maximum which probably lies between 6140 and 6430Å. The spectrum at longer wave-lengths is banded, the absorption coefficients of the bands having very low values.⁸ The edges of the bands converge to a limit at 4785Å, the absorption being continuous at shorter wave-lengths.⁹ It is only in the continuous region that the absorption coefficients attain large values. Here the molecule is dissociated into one normal chlorine atom and one bearing an energy of excitation of 0.109 volt.¹⁰ Since the maximum absorption occurs at a wave-length much shorter than the convergence limit, the excess energy of the light must appear as large amounts of kinetic energy possessed by the dissociated atoms.

The second absorption region extends from about 1900 to 1560Å and is entirely continuous.¹¹ It corresponds to a dissociation similar to that produced by absorption in the region of longer wave-lengths, except that the atoms produced are endowed with greater kinetic energies. From these considerations it is evident that the primary process in the hydrogen-chlorine combination must consist in the formation of chlorine atoms when the mixture of gases is irradiated with wave-lengths shorter than 4785Å.

To account for various features of the photochemical reaction anomalies of absorption have been assumed. Statements that the absorption by chlorine is dependent upon the intensity of the incident light¹² could not be confirmed by Gray and Style.¹³ For a long period water was believed necessary for the photochemical reaction between hydrogen and chlorine. It was stated that the disposition of energy absorbed by moist and by dry samples of chlorine is different.¹⁴ No difference in absorption was observed by v. Halban and Siedentopf, Kistiakowsky¹⁵ or Kornfeld and Steiner.¹⁶ Furthermore, no fluorescence could be detected within the continuous region.

Budde Effect. A phenomenon which excited considerable interest and which at one time appeared important for the explanation of the mechanism of the hydrogen-chlorine combination was the observation by Budde¹⁷ that chlorine gas expands when illuminated by white or blue light but not when red or yellow light is employed. He found the expansion the result of a temperature increase, an observation confirmed by Bevan.¹⁸ Richardson¹⁹ found the expansion to be roughly proportional to the intensity of the light employed. The effect is usually attributed to heat liberated as a result of the recombination of chlorine atoms formed by the absorption within the continuous region. The effects of small amounts of moisture on the extent of this effect have been discussed since the observations of Shenstone,²⁰ who found pure dry chlorine to give only a very small Budde effect. This effect could be increased by the admission of some moisture.²¹

⁷ v. Halban, H., and Siedentopf, K., *Z. physik. Chem.*, **103**, 71 (1922).

⁸ Kuhn, H., *Z. Physik*, **39**, 77 (1926).

⁹ Elliott, A., *Proc. Roy. Soc.* **123**, 629 (1929); **127**, 638 (1930).

¹⁰ Birge, R. T., *Phys. Rev.*, **35**, 133 (1930).

¹¹ Cordes, H., and Sponer, H., *Z. Physik*, **63**, 334 (1930).

¹² Weigert, F., and Brodmann, L., *Z. physik. Chem.*, **106**, 426 (1923).

¹³ Gray, L. T. M., and Style, D. W. G., *Proc. Roy. Soc.* **126A**, 603 (1930).

¹⁴ Mellor, J. W., *J. Chem. Soc.*, **81**, 1280 (1902).

¹⁵ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

¹⁶ Kornfeld, G., and Steiner, W., *Z. Physik*, **45**, 325 (1927).

¹⁷ Budde, E., *J. prakt. Chem.*, **7**, 376 (1873).

¹⁸ Bevan, P. V., *Phil. Trans.*, **202**, 90 (1904).

¹⁹ Richardson, A., *Phil. Mag.*, **32**, 221, 277 (1891).

²⁰ Shenstone, W. A., *J. Chem. Soc.*, **71**, 471 (1897).

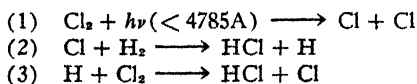
²¹ See also Ludlam, E. B., *Proc. Roy. Soc. Edinburgh*, **34**, 197 (1924).

Kistiakowsky²² attributed the water dependence of the effect to the necessity for inert molecules to carry off the energy of recombination of chlorine in three-body collisions. In the absence of water, the free chlorine atoms could combine only on the glass walls of the vessel. The large heat capacity and relatively good heat conductance of the vessel would, however, prevent the heating of the gas and so the Budde effect would be missed. On the other hand, Martin, Cole and Lent²³ and more recently, Kistiakowsky²⁴ have denied the effect of drying in lessening the photoexpansion of chlorine. Narayana,²⁵ however, states that the Budde effect cannot be observed in dry gases, unless the vessel is carefully vacuum-insulated. In accordance with the theory that a primary dissociation is essential, the effect is absent in chlorine illuminated by wave-lengths greater than 5000Å and in bromine above 5500Å. It varies as the pressure of the halogen and as the square root of the intensity of the light.

In the case of bromine, Lewis and Rideal²⁶ have advanced evidence in support of a different mechanism. They believed a bromine-hydrate (heat of formation 1.09 kcal.) to be dissociable by wave-lengths 5700-5400Å, in the band rather than in the dissociation region of the spectrum. Thus the bromine hydrate could be dissociated by wave-lengths longer than those required for the dissociation of dry bromine. Recombination of the bromine and water was held to give rise to the heat which produces the characteristic expansion. Matthews²⁷ has found drying to lessen somewhat the Budde effect, although it could not be entirely eliminated in this manner.

MECHANISM OF THE HYDROGEN-CHLORINE COMBINATION

The outstanding characteristic of the hydrogen-chlorine combination is the high quantum yield. Bodenstein²⁸ calculated that, were it possible to eliminate traces of inhibiting oxygen from the chlorine employed, the yield should be approximately 10^6 . Kornfeld and Müller²⁹ found it to be 1.10×10^5 for light of 4360Å. Harris³⁰ has, by using blue light and very carefully purified gases, obtained a value of 6×10^5 and Bodenstein and Winter³¹ of 4.2×10^6 in silver vessels. This corresponds to an average chain duration of 16 seconds. Obviously, such quantum yields require a chain mechanism and many have been proposed. At this point, mention of the mechanism which apparently is most favored, will be made and discussion of the effects of inhibitors will be postponed until the experimental data have been discussed. The primary process is a photodissociation of the chlorine into atoms. The subsequent reactions which form the chain were first suggested by Nernst.³²



Rodebush and Klingelhöfer³³ have advanced more cogent evidence than that originally suggested by Nernst for the thermodynamic possibility of reaction (2), although they believe that only every 10^6 th collision leads to reaction. The acti-

²² Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2199 (1927).

²³ Martin, W. H., Cole, A. F. W., and Lent, E. E., *J. Phys. Chem.*, **33**, 148 (1929).

²⁴ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **51**, 1395 (1929).

²⁵ Narayana, T. S., *Indian J. Physics*, **9**, 91 (1934); *Chem. Abs.*, **29**, 684 (1935).

²⁶ Lewis, B., and Rideal, E. K., *J. Chem. Soc.*, 583, 596 (1926).

²⁷ Matthews, E., *Trans. Faraday Soc.*, **25**, 41 (1929); cf. Ritchie, M., and Ludlam, E. B., *J. Chem. Soc.*, 1680 (1937).

²⁸ Bodenstein, M., *Z. physik. Chem.*, **85**, 351 (1913).

²⁹ Kornfeld, G., and Müller, H., *Z. physik. Chem.*, **117**, 242 (1925).

³⁰ Harris, L., *Proc. Nat. Acad. Sci.*, **14**, 110 (1928).

³¹ Bodenstein, M., and Winter, E., *Sitzber. preuss. Akad. Wiss., Physik-math. Kl.*, **2** (1936).

³² Nernst, W., *Z. Elektrochem.*, **24**, 335 (1918).

³³ Rodebush, W. H., and Klingelhöfer, W. C., Jr., *Proc. Nat. Acad. Sci.*, **18**, 531 (1932); *J. Am. Chem. Soc.*, **55**, 130 (1933).

³⁴ Marshall, A. L., *J. Phys. Chem.*, **29**, 842 (1925).

vation energy is 6.1 kcal. Marshall³⁴ calculated for reaction (2) a free energy change of approximately zero. Reaction (3) is believed by Bodenstein to occur at each hundredth collision. Since it regenerates a free chlorine atom, the chain mechanism would be readily apparent did reaction (2) occur.

Many efforts were made to demonstrate experimentally the occurrence of reaction (2), including the work of Jost and Schweitzer.³⁵ Could this reaction be admitted, it is apparent that the great difference between the hydrogen-bromine and the hydrogen-chlorine combinations would be readily explicable. The failure of many direct attempts to show experimental proof for reaction (2), however, delayed for several years the acceptance of the simple Nernst chain mechanism and led to the proposal of a number of alternative mechanisms which attempted to avoid the use of this reaction. Included among these proposals were the presence of excited chlorine molecule chains or of chains carried by excited HCl or by a postulated triatomic chlorine molecule.

Attempts to activate chlorine by a brush electric discharge or by a mercury lamp so that when conducted into unilluminated hydrogen the two substances would produce hydrogen chloride were made (unsuccessfully) by Wendt.³⁶ Other unsuccessful attempts were described by Bodenstein and Taylor³⁷ and by Marshall.³⁸ Jost and Schweitzer were able to demonstrate the reaction (2) by passing a very rapid stream of irradiated chlorine into hydrogen. The free atoms, however, recombine rapidly on the walls of the conducting tube and the experiment fails when the irradiated gas remains in the tube longer than 10^{-4} second. Nevertheless, with the demonstration of the possibility of the reaction, the Nernst chain becomes admissible. It is thus conceivable that there can be a long-continued interplay of reactions (2) and (3) leading to the production of large numbers of molecules of hydrogen chloride consequent upon the absorption of one quantum of light, before the free atoms which carry the chains are lost by wall reactions or by interactions with impurities, *e.g.*, oxygen.

History of the Work on the Reaction. That a mixture of hydrogen and chlorine explodes in bright sunlight and reacts slowly in diffused light was first observed by Cruikshank.³⁹ Quantitative rate measurements, the first on any photochemical change, were made by Draper⁴⁰ by means of a "tithonometer." In this apparatus the hydrogen chloride produced was absorbed in water, and the volume contraction was followed by the movement of a column of liquid along a capillary. Draper found indigo rays the most powerful in causing the contraction, as did Favre and Silbermann.⁴¹

In the course of this work what has come to be known as the Draper effect⁴² was discovered. This consists of a brief expansion on exposure to light, followed by a period in which there is no pressure change, and then by a contraction. The details of the Draper effect were studied by Mellor and Anderson,⁴³ Bevan,⁴⁴ and by Weigert and Kellerman.⁴⁵ Bevan, who could produce the Draper effect only by use of fairly intense light, attributed the effect to a rise of temperature accompanying the formation of

³⁵ Jost, W., and Schweitzer, H., *Z. physik. Chem.*, **13B**, 373 (1931).

³⁶ Wendt, G. L., *Chem. Met. Eng.*, **24**, 83 (1921); Wendt, G. L., Landauer, R. S., and Ewing, W. W., *J. Am. Chem. Soc.*, **44**, 2377 (1922). See, however, Venkataramaiah, Y., *J. Phys. Chem.*, **27**, 74 (1923).

³⁷ Bodenstein, M., and Taylor, H. S., *Z. Elektrochem.*, **22**, 202 (1916).

³⁸ Marshall, A. L., *J. Phys. Chem.*, **30**, 757 (1926).

³⁹ Cruikshank, W., *Nicholson's J.*, **5**, 202 (1801).

⁴⁰ Draper, J., *Phil. Mag.*, **19**, 195 (1841); **23**, 40 (1843); **25**, 237 (1844).

⁴¹ Favre, P. A., and Silbermann, J. T., *Ann. chim. phys.*, **37**, 497 (1853). Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2694, 2709 (1930); 157 (1934)] find the violet region the most effective.

⁴² Draper, J., *Phil. Mag.*, **26**, 476 (1845).

⁴³ Mellor, J. W., and Anderson, W. R., *J. Chem. Soc.*, **81**, 414 (1902).

⁴⁴ Bevan, P. V., *Phil. Trans.*, **202**, 81 (1904).

⁴⁵ Weigert, F., and Kellerman, K., *Z. physik. Chem.*, **107**, 1 (1924).

hydrogen chloride. Weigert made a detailed study of the time relations involved, employing a photographic Töpler cloud method depending upon local changes of refractive index. The magnitude of the effect was related to the degree of drying of the gases. The cloud observed when a mixture of chlorine and electrolytic gas was irradiated with light of short wave-length paralleled the Draper effect in time-intensity relations. The cloud was assumed due to a warming of the gas and the amount of thermal expansion corresponded with the calculated amount of heat which is liberated during the production of the hydrogen chloride. Weigert's theory of clustering about a group of two molecules between which an electron has passed from the hydrogen molecule to the chlorine molecule did not prove significant. His experimental observation that the change in density did not begin until 10^{-4} second after irradiation by a single spark discharge and attained its maximum only some hundredths of a second after the irradiation gave direct evidence for the existence of a chain reaction.

Induction Period. Bunsen and Roscoe made studies of the rate of the reaction; an improved "actinometer" was used for correlating the reaction rate and the light intensity.⁴⁶ In the course of this work they described in detail an earlier observed induction period to which they ascribed unwarranted *general* photochemical significance. The details given by them and by later workers⁴⁷ were confusing and indicated the induction period to be dependent on the length of the gas column irradiated, the intensity of the light, the temperature and the previous history of the gas. The interpretation of the results was further complicated by the belief of Bunsen and Roscoe that the absorption of the gases during reaction is increased over that of unreacting gases, a view now known to have been erroneous. The simple explanation that the induction period is due to the presence of small amounts of inhibiting impurities which are destroyed in large part during the inert period was established by Burgess and Chapman.⁴⁸ They found no difference in the extinction of irradiated and non irradiated gas mixtures. Also, oxygen did not affect the length of the induction period, and traces of ammonia could produce very long induction periods, the duration of which varied directly as the concentration of the added ammonia. A later suggestion by Chapman and McMahon⁴⁹ that the inhibition should be attributed to the production of NCl_3 by the interaction of chlorine with the ammonia was, however, considered untenable by Norrish.⁵⁰ Norrish advanced the view that the ammonia derived from the impurities was adsorbed on the surface of the vessel, poisoning the latter for certain surface reactions involving a water-chlorine compound. Arguments were raised against this theory by Cathala⁵¹ Griffiths and Norrish⁵² have accepted the view that the induction period is due to the formation of NCl_3 , which undergoes photosensitized decomposition in the presence of excess chlorine by short reaction chains. The quantum efficiency of this reaction falls to about two as the chlorine pressure is increased.

Nitric oxide (but not nitrous oxide) and chlorine dioxide also inhibit the reaction.⁵³ Oxygen apparently slows the rate of the reaction rather than causes an induction period. The effect of oxygen in inhibiting the reaction is not attended by its total disappearance, as is that of the inhibitors responsible for the

⁴⁶ Bunsen, R., and Roscoe, H., *Pogg. Ann.*, **96**, 373 (1855); **100**, 193, 483 (1857); **101**, 32, 237, 275 (1857); **108**, 193 (1859), **117**, 531 (1862); Reprinted in *Ostwald's Klassiker*, No. 34 and 38 (1892).

⁴⁷ Pringsheim, E., *Wied. Ann.*, **32**, 384 (1887); Mellor, J. W., *J. Chem. Soc.*, **81**, 1292 (1902).

⁴⁸ Burgess, C. H., and Chapman, D. L., *J. Chem. Soc.*, **89**, 1399 (1906).

⁴⁹ Chapman, D. L., and McMahon, P. S., *J. Chem. Soc.*, **95**, 1717 (1909); **97**, 847 (1910).

⁵⁰ Norrish, R. G. W., *J. Chem. Soc.*, **127**, 2316 (1925).

⁵¹ Cathala, J., *Bull. Soc. Chim.*, **39**, 612 (1926).

⁵² Griffiths, J. G. A., and Norrish, R. G. W., *Trans. Faraday Soc.*, **27**, 451 (1931); *Proc. Roy. Soc.*, **147A**, 140 (1934).

⁵³ Chapman, D. L., and McMahon, P. S., *J. Chem. Soc.*, **95**, 959 (1909).

induction period. The rate of the formation of hydrogen chloride has been found to be inversely proportional to the oxygen concentration, at least over the range, 0.09 to 1.00 per cent.⁵⁴

Effects of Water Vapor. From the earliest to the most recent studies, attention has been directed to the effects of traces of water vapor on the hydrogen-chlorine combination. Baker⁵⁵ claimed that under conditions of extreme dryness, the reaction proceeds only very slowly in direct sunlight, but Mellor and Russell⁵⁶ found that even these extremely dry mixtures could be made to explode by an electric spark. Bodenstein and Dux⁵⁷ found the rate of combination of the gases to be unaffected by drying down to a water vapor pressure of 10^{-3} mm. of mercury. Tramm,⁵⁸ however, found that drying by a special liquid air technique prevented the combination from occurring in sunlight. Coehn and Jung⁵⁹ claimed that the photochemical reaction was prevented when the water vapor pressure was reduced below 10^{-7} mm. and visible light was the source employed. When the effective light was of wave-length shorter than about 2540A the reaction was not prevented by drying, although the quantum yield was lowered to about eight. On the basis of these results, Norrish⁶⁰ advanced the theory that water is required as a catalyst

in the primary process. He believed an intermediate compound $\begin{array}{c} \text{H} \\ | \\ \text{H} > \text{O} < \text{Cl} \\ | \\ \text{Cl} \end{array}$ to be formed and adsorbed on the walls of the vessel where subsequent reaction occurs. Coehn's explanation of the effect of water (an effect due to water in atomic chlorine reactions) appeared inadequate both to Norrish and to Cathala.⁶¹ The latter worker, however,⁶² was unable to accept the theory of Norrish. Kistiakowsky,⁶³ pointed out that the theory of Norrish had been disproved by the experiments of Coehn and Heymer⁶⁴ in which a chlorine and hydrogen mixture reacted on exposure to radiation in apparatus arranged to minimize solid and liquid surfaces. For a time it was believed that water might be required to enable the absorption of radiation by chlorine leading to dissociation of the latter into atoms.⁶⁵

As the spectroscopic evidence on the dissociation process gained prominence, it became necessary to discard such views. The effect of water vapor was next attributed to some possible influence exerted by it on the rate of recombination of free chlorine atoms.⁶⁶ Recently, however, in view of the inadequacy of the explanations which could be advanced to explain the mechanism by which water vapor aids the reaction, the tendency has been to reexamine the validity of the phenomenon. Particularly is this necessary, since it would be very difficult to explain why water vapor should have a greater effect upon chlorine atoms produced by visible radiations than by shorter rays as had been claimed by Coehn and Tramm. Bodenstein

⁵⁴ Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913).

⁵⁵ Baker, H. B., *J. Chem. Soc.*, **65**, 612 (1894).

⁵⁶ Mellor, J. W., and Russell, E. J., *J. Chem. Soc.*, **81**, 1272 (1902).

⁵⁷ Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913).

⁵⁸ Tramm, H., *Z. physik. Chem.*, **105**, 356 (1923).

⁵⁹ Coehn, A., and Jung, G., *Ber.*, **56**, 696 (1923).

⁶⁰ Norrish, R. G. W., *J. Chem. Soc.*, **127**, 2316 (1925); *Trans Faraday Soc.*, **21**, 575 (1925).

⁶¹ Cathala, J., *Compt. rend.*, **181**, 33 (1925).

⁶² Cathala, J., *Bull. Soc. Chim.*, **39**, 612 (1926).

⁶³ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

⁶⁴ Coehn, A., and Heymer, G., *Naturwiss.*, **14**, 299 (1926); *Ber.*, **59B**, 1794 (1926).

⁶⁵ Lewis, B., *Nature*, **120**, 473 (1927); Weigert, F., *Z. physik. Chem.*, **106**, 426 (1923). Ichikawa, T., *Z. physik. Chem.*, **10B**, 299 (1930).

⁶⁶ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

and Bernreuther⁶⁷ suggest that the earlier observations may have been due to the accidental introduction of strong inhibitors such as metal chlorides in the drying methods employed. The work of Rollefson and Potts⁶⁸ indicates that at low temperatures at least, the presence of water vapor has no marked effect on the rate of the reaction.

Development of Chain Mechanisms. The first chain mechanism suggested by Bodenstein involved an ionized chlorine molecule⁶⁹ but this was soon shown to be excluded⁷⁰ by the observations that no ionization occurs in irradiated chlorine gas,⁷¹ or during the photocombination of hydrogen and chlorine.⁷² Bodenstein⁷³ next proposed a mechanism in which the chains were assumed to be carried both by activated chlorine and activated hydrogen chloride molecules, a view supported in principle (although not in the details of chain propagation) by Stern and Volmer.⁷⁴

The dissociation theory of Nernst⁷⁵ was proposed in 1918; many attempts followed to decide between the "hot molecule" and the dissociation theories. Attempts to compare rates and quantum yields of light and α -ray induced reactions⁷⁶ failed to afford a basis for a decision. Much labor was devoted to efforts to settle the question by kinetic studies. The earlier attempts were also equivocal, and it became evident that with sufficient ingenuity the kinetic data obtained under various experimental conditions might be interpreted with some degree of success by employing the concepts of either theory. The details of the many proposed mechanisms, some of which involved as many as eleven reaction constants (for the most part undetermined or undeterminable) cannot be given here.

REACTION KINETICS^{76a}

Contrary to Baly and Barker,⁷⁷ more recent observers find the rate of the formation of hydrogen chloride proportional to the light intensity.⁷⁸ Rollefson found the rate of formation also proportional to the hydrogen and chlorine⁷⁹ concentrations. He reasoned that if the reaction were due to excited molecules, the velocity constant should decrease rapidly at low pressures, since the time between collisions would then be long enough to permit the excitation energy to be lost by fluorescence. Should the reaction be due to free atoms, the rate constant should be independent of the pressure. From kinetic considerations and from the probable life of an excited chlorine molecule, he calculated that it should be possible

⁶⁷ Bodenstein, M., and Bernreuther, F., *Berl. Preuss. Akad. Wiss., Phys. math. Klasse*, 333 (1933); *Chem. Abs.*, 27, 3669 (1933).

⁶⁸ Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, 55, 860 (1933).

⁶⁹ Bodenstein, M., *Z. physik. Chem.*, 85, 329 (1913).

⁷⁰ LeBlanc, M., and Volmer, M., *Z. Elektrochem.*, 20, 494 (1914).

⁷¹ Ludlam, E. B., *Phil. Mag.*, 23, 757 (1912).

⁷² Thomson, J. J., *Proc. Cambr. Phil. Soc.*, 11, 901 (1901).

⁷³ Bodenstein, M., *Z. Elektrochem.*, 22, 53 (1916).

⁷⁴ Stern, O., and Volmer, M., *Z. wiss. Phot.*, 19, 275 (1920).

⁷⁵ Nernst, W., *Z. Elektrochem.*, 24, 335 (1918).

⁷⁶ Bodenstein, M., *Z. Elektrochem.*, 22, 53 (1916); Taylor, H. S., *J. Am. Chem. Soc.*, 37, 24 (1915); 38, 280 (1916). Porter, F., Bardwell, D. C., and Lind, S. C., *J. Am. Chem. Soc.*, 48, 2603 (1926).

^{76a} For the evaluation of the various rate constants, see Taylor, H. S., *J. Phys. Chem.*, 42, 789 1453

⁷⁷ Baly, E. C. C., and Barker, W. F., *J. Chem. Soc.*, 119, 653 (1921).

⁷⁸ Chapman, M. C. C., *J. Chem. Soc.*, 125, 1521 (1924); Marshall, A. L., *J. Phys. Chem.*, 29, 1453 (1925); Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693 (1930). Rollefson, G. K., *J. Am. Chem. Soc.*, 51, 770 (1929); Bateman, J. B., and Craggs, H. C., *Trans. Faraday Soc.*, 27, 445 (1931); Bodenstein, M., and Unger, W., *Z. physik. Chem.*, 11B, 253 (1930); see, however, Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1869 (1937).

⁷⁹ See, however, Bodenstein, M., and Dux, W., *Z. physik. Chem.*, 85, 297 (1913); Thon, N., *Z. physik. Chem.*, 124, 327 (1926). For the influence of oxygen on the rate, see Chapman, M. C. C., *loc. cit.*; Norrish, R. G. W., and Rideal, E. K., *J. Chem. Soc.*, 127, 787 (1925).

to distinguish between these mechanisms at a hydrogen pressure of one millimeter. His data showed no change in the rate constant as the pressure was decreased below this limit and therefore afforded support for the dissociation mechanism.

Recently efforts have been directed toward an understanding of the manner in which, in pure gases, the chains are broken by the removal of the atoms. Reactions at the wall were suggested by Chapman and Grigg⁸⁰ for destroying the catalyst (the nature of which then was not considered) since the reaction was slower in capillary tubes than when conducted under the same light intensity in tubes of wider bore. Trifonoff,⁸¹ who suggested that grease on the stopcocks might start the reaction, believed that recombination of atoms diffused to the walls at low pressures might break the chains. At pressures above 30 mm., he believed the processes to occur chiefly in the free space, but below 10 mm. practically all of the chains break down at the surfaces of the walls. Bodenstein and Unger were also of the opinion that at higher pressures the chains must be broken by some compound present in the reaction space. A volatile deposit, possibly of a silicon oxychloride, has been detected on the walls of vessels in which free chlorine atoms had been produced. Hertel⁸² thought that this might be responsible for breaking the chains, since the rate of formation of hydrogen chloride could be lowered by carrying out the reaction in vessels in which chlorine had previously been irradiated. He had found that the rate⁸³ might be expressed by $k_1(\text{H}_2)(\text{Cl}_2)^2$ when the chlorine is present in great excess and by $k_2(\text{H}_2)^2(\text{Cl}_2)$ when the hydrogen is in great excess. He also gave a more general equation, which need not be reproduced here. Hertel believed that the observed rate could be accounted for on the assumption that oxygen terminates the chains by combining with the hydrogen atoms. Chapman and Gibbs⁸⁴ find the rate of the reaction proportional to the square root of the intensity of the light when the chlorine used has been very carefully freed from oxygen and other inhibiting impurities.

Behavior at very low pressures similar to that found by Rollefson has also been reported by Allmand and Craggs,⁸⁵ the reaction proceeding at the normal rate even at chlorine pressures as low as 0.012 mm. Water vapor also failed to affect the rate except at low total pressures. They stated that at total pressures of 2 mm. ultraviolet light affords lower quantum yields than does visible light, but this difference is not observed at higher pressures. It was thought that it might be accounted for by the formation of triatomic chlorine molecules by the ultraviolet of short wave-length. By quantum mechanical considerations, Rollefson and Eyring⁸⁶ concluded that, for all the halogens, molecules of the type X_3 are stable at room temperatures with respect to dissociation into X_2 and X . Cremer⁸⁷ had previously suggested the possibility that this molecule might function as a chain carrier, as had Cathala⁸⁸ who called it "chlorozone."⁸⁹

⁸⁰ Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

⁸¹ Trifonoff, A., *Z. physik. Chem.*, 3B, 195 (1929); 6B, 118 (1929); Trifonoff, A., and Ryabinin, G., *Trans. State Phys.-Tech. Lab. (Moscow)*, No. 14, 26 (1930); *Chem. Abs.*, 24, 1297 (1930).

⁸² Hertel, E., *Z. physik. Chem.*, 15, 325 (1932).

⁸³ Hertel, E., *Z. physik. Chem.*, 14B, 443 (1931).

⁸⁴ Chapman, D. L., and Gibbs, F. B., *Nature*, 127, 854 (1931).

⁸⁵ Allmand, A. J., and Craggs, H. C., *Nature*, 130, 927 (1932); *J. Chem. Soc.*, 241 (1936); 1889 (1937). Craggs, H. C., Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1878 (1937).

⁸⁶ Rollefson, G. K., and Eyring, H., *J. Am. Chem. Soc.*, 54, 170 (1932).

⁸⁷ Cremer, E., *Z. physik. Chem.*, 128, 285 (1927).

⁸⁸ Cathala, J., *J. chim. Phys.*, 25, 182 (1928).

⁸⁹ For further discussion of chain carriers for this reaction see Göhring, R., *Z. Elektrochem.*, 27, 516 (1921); Chapman, D. L., *Trans. Faraday Soc.*, 21, 547 (1925) and Warburg, E., *Z. Elektrochem.*, 27, 139 (1921).

⁹⁰ Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, 20B, 420 (1933).

Allmand and Craggs state that the presence of 0.1 mm. of oxygen retards the reaction between chlorine and less than 0.01 mm. of hydrogen. It has no effect, however, when there is 0.01 to 0.5 mm. of hydrogen, but under these conditions the oxygen is consumed.

Results of Bodenstein and Schenk⁹⁰ on the relative yields of hydrogen chloride and of water in streaming mixtures of chlorine, hydrogen and oxygen at 60°C. have been criticized by Chapman and Watkins,⁹¹ who employed mixtures rich in oxygen. Ritchie and Norrish,⁹² who determined the reaction rate by measuring the chlorine absorption, found hydrogen chloride to have a pronounced inhibiting effect on mixtures which contained oxygen. In the absence of oxygen, the quantum efficiency is given by the expression

$$\frac{2.8 \times 10^8 (H_2) (Cl_2)}{(Cl_2) + 1.7 (HCl) (I_{abs})^{0.4}}$$

Their maximum quantum yield was 1.2×10^5 . The velocity of hydrogen chloride formation varies with the 0.6 power of the intensity of the absorbed light in approximate agreement with Chapman and Gibbs. Reaction chains are terminated mainly by self-neutralization.⁹³ In the presence of oxygen, both hydrogen chloride and hydrogen have inhibiting effects, that of the former being four times that of the latter. With increasing hydrogen pressures, the quantum efficiency rises through a maximum. For mixtures rich in oxygen, it varies inversely as the oxygen pressure and is independent of the light intensity. The quantum efficiency is also reduced by inert gases.⁹⁴ At low concentrations of oxygen, it shows a dependence on the light intensity.

According to Krauskopf and Rollefson,⁹⁵ as the ratio of oxygen to chlorine is increased, the ratio of the production of water to that of hydrogen chloride approaches a limit between one and two. From its temperature dependence, the activation energy for the reactions yielding hydrogen chloride appears to be greater than that for those yielding water. They hold that the existence of the limit for the ratio of the two products shows that the Nernst chains must be terminated by a reaction $H + O_2 \rightarrow HOO_2$ rather than by $Cl + O_2 \rightarrow ClO_2$. Rollefson and Potts⁹⁶ state that at temperatures below 172°K., the melting point of chlorine, the rate depends on the square root of the light absorbed. From the temperature coefficients, observed at 3600Å, the heat of activation is 5.8 kcal. At low temperatures the value 4.6 kcal. is, however, found. They accept the suggestion that a volatile silicon oxychloride terminates the chains. They suggest further that the large inhibiting effect of hydrogen chloride observed by Norrish and Ritchie may have been due to the introduction of an inhibiting impurity in the hydrogen chloride added. The rate equation given by Rollefson and Potts is said to be valid at temperatures as low as 200°K. The equation is:

$$\frac{d(HCl)}{dt} = k I_{abs} (H_2) \frac{1}{1 + k_1 \frac{(HCl)}{(Cl_2)}},$$

⁹¹ Chapman, D. L., and Watkins, J. S. *J. Chem. Soc.*, 743 (1933)

⁹² Ritchie, M., and Norrish, R. G. W., *Proc. Roy. Soc.*, 140, 99, 112, 713 (1933).

⁹³ See also Tamura, M., *Rev. Phys. Chem. Japan*, 11, 1 (1937); *Chem. Abs.*, 32, 1184 (1938).

⁹⁴ Ritchie, M., *J. Chem. Soc.*, 857 (1937)

⁹⁵ Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, 56, 327 (1934); see also Ritchie, M., *J. Chem. Soc.*, 857 (1937).

⁹⁶ Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, 57, 1027 (1935).

in which $k_1 \leq 0.1$. Some of the proposed chain mechanisms have been discussed by Bates.⁹⁷ An interesting direct method of demonstrating the existence of a chain reaction has been the application of the para-hydrogen test for the presence of free hydrogen atoms,⁹⁸ to which reference has been made in a preceding chapter. Kokochashvili⁹⁹ has studied the reaction by the aid of very brief irradiations (.08 second) of high intensity secured by magnesium flashes, and has discussed his results from the standpoint of chain mechanisms. Deuterium molecules are less reactive than hydrogen, the activation energy being slightly higher for the former.¹⁰⁰ Farkas and Farkas¹⁰¹ find the reaction with deuterium to proceed at one-third the rate of that with hydrogen. They ascribe the difference in rates to the larger zero-point energy of hydrogen as compared with deuterium. The calculated additional activation energy of 0.8 kcal. required by deuterium agrees well with the difference in zero-point energy between H^1_2 , HD and D_2 of 810 and 1710 cal.

THRESHOLDS AND THE EFFECTS OF WAVE-LENGTHS

Within the continuous region, Bodenstein and Schenk¹⁰² found the quantum yield to be independent of the wave-length. Allmand and Beesley,¹⁰³ using filters, gave the following *relative* values: 2600A, 0.10; 3130A, 0.49; 3650A, 0.53; 4050A, 1.00; 4360A, 0.67 and 5460A, 0.22. On the other hand, Bateman and Allmand¹⁰⁴ found the quantum yield independent of the wave-length between 4000A and 4900A, but observed it to fall slowly on either side of this region. The earlier results were attributed to the accidental use of a glass window. A result at 4920A was considered anomalous since the ratio between the yield at this wave-length and that at 4050A rose on prolonged irradiation from an initial value of 0.6 to a constant value of about 8. Between 4000 and 2900A the yield was of constant order of magnitude, but appeared to fall off by about 10-20 per cent in going from the visible toward the shorter wave-lengths.¹⁰⁵ The observation that a definite reaction can take place at 5400-5500A is of interest in view of earlier discussions (Chapter 15) regarding the existence of a threshold wave-length for this reaction.¹⁰⁶

Hertel assumed the primary process to be the formation of excited chlorine molecules under the influence of light in the band region. A small fraction of these molecules is then dissociated by impact with molecules of either hydrogen, chlorine or of hydrogen chloride. The efficiencies of these molecules in effecting dissociation were found to be in the ratio of 1:3:0.5. As a result of this dissociation, chains are set up as in the continuous region. The quantum yield in the region between 4850 and 5090A was found to be about half that observed by light in the continuous region. Hertel believed it would be very difficult to determine whether the reaction could proceed at wave-lengths longer than 5000A since the absorption is so low in this region. He noted that Dhar and Bhagwat had found a limiting zone at 6650A, and believed that a slight reaction might occur at 7700A.

⁹⁷ Bates, J. R., *Proc. Nat. Acad. Sci.*, 19, 81 (1933).

⁹⁸ Geib, K. H., and Harteck, P., *Z. physik. Chem.*, 15B, 116 (1931).

⁹⁹ Kokochashvili, V., *Z. physik. Chem.*, 23B, 431 (1933)

¹⁰⁰ Rollefson, G. K., *J. Chem. Physics*, 2, 144 (1934).

¹⁰¹ Farkas, L., and Farkas, A., *Naturwiss.*, 22, 218 (1934).

¹⁰² Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, 20B, 420 (1933).

¹⁰³ Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693, 2709 (1930).

¹⁰⁴ Bateman, J. B., and Allmand, A. J., *J. Chem. Soc.*, 157 (1934).

¹⁰⁵ See also Norrish, R. G. W., and Ritchie, M., *Proc. Roy. Soc.*, 140, 99, 112, 713 (1933)

¹⁰⁶ Hertel, E., *Z. physik. Chem.*, 14, 443; 15, 325 (1932).

Recently Allmand and Craggs¹⁰⁷ have found it possible to form hydrogen chloride when mixtures of 0.1-0.6 mm. of hydrogen and 1.7 to 166 mm. of chlorine are irradiated with light of 5460A, a slightly longer wave-length than corresponds to the dissociation of chlorine into normal atoms. It would be expected that if excited molecules are formed and dissociated on impact with other molecules the absorbed energy of excitation must supply most of the energy for the subsequent dissociation. The slight deficiency involved when 5460A is used can, however, be supplied otherwise. If the chlorine molecules which absorb this energy are initially in high vibrational levels they can acquire sufficient energy by the absorption of this wave-length. The results could, it was believed, be correlated with the continuous background of the banded absorption spectrum of chlorine. No reaction occurred at 5790A. From the temperature coefficient of the reaction at 5460A, the activation energy appeared to be 9.78 kcal. The quantum efficiency relative to unity at 4360A was approximately 0.3. Subsequent to a more recent interpretation of the continuous absorption spectrum of chlorine, Bayliss has shown that at all wave-lengths the primary process is the same—dissociation—and that the quantum yield, temperature coefficient and activation energy are independent of the wave-length of the exciting radiation.¹⁰⁸

In addition to the investigations in which temperature coefficients have been determined for calculations of activation energies, there have been a few earlier observations of temperature coefficients to which very brief reference may be made. Padoa and Butironi¹⁰⁹ seem to have been the first to make such determinations. They found the acceleration produced by increase in temperature to be but small in the ultraviolet, greater for violet and blue light and a maximum for green light. The values were: green (5500-5300A), 1.50; blue (4900-4700A), 1.31; violet (4600-4400A), 1.21; ultraviolet (4000-3500A), 1.17. Hertel's observations gave 1.48 in the band region in good agreement with those of Padoa. The values obtained by Livingston and Lind¹¹⁰ were somewhat lower.

Lavrov¹¹¹ has made many determinations of the critical pressures at which the carbon arc will ignite various mixtures of chlorine, hydrogen and various gases.

¹⁰⁷ Allmand, A. J., and Craggs, H. C., *J. Chem. Soc.*, 241 (1936).

¹⁰⁸ Aickin, R. G., and Bayliss, N. S., *Trans. Faraday Soc.*, 33, 1333 (1937); Bayliss, N. S., *Ibid.*, 33, 1339 (1937).

¹⁰⁹ Padoa, M., and Butironi, C., *Atti accad. Lincei*, 24 (II), 215 (1916); *Chem. Abs.*, 11, 1356 (1917).

¹¹⁰ Livingston, R., and Lind, S. C., *J. Am. Chem. Soc.*, 52, 593 (1930).

¹¹¹ Lavrov, F. A., and Zagulin, A. V., *Acta Physicochim. U.R.S.S.*, 1, 979 (1934); *Brit. Chem. Abs.*, A, 943 (1936); Lavrov, F. A., and Perel'man, T., *Acta Physicochim. U.R.S.S.*, 2, 91 (1935); *Chem. Abs.*, 29, 6506 (1935).

Chapter 19

Reactions of Inorganic Gases Other than Halogen Halides

REACTIONS OF OXYGEN

The Oxygen-Ozone Transformation. Schönbein, who was the discoverer of ozone, reported that oxygen can be photochemically activated¹ and Nernst² interpreted the formation of ozone by the silent electric discharge as a photochemical reaction. Lenard³ observed formation of ozone in air by the action of sparks from a Leyden jar and demonstrated that it was due to light of wave-lengths less than 2000Å. Goldstein⁴ succeeded in preparing a dark blue liquid containing a high percentage of ozone within a discharge tube containing oxygen and immersed in liquid air.

With the advent of quartz mercury arcs, reports began to appear regarding the conditions under which a considerable yield of ozone could be produced in air by ultraviolet radiations. Fischer and Braehmer⁵ described an apparatus in which electrolytic gas was conducted through an annular narrow space surrounding a quartz-contained mercury arc, the entire apparatus being cooled by immersion in water. Their measurements of the yield of ozone produced under different conditions of operation indicated its formation to be opposed by a reverse reaction, the speed of the latter increasing rapidly with rise of temperature. Warburg and Regener⁶ had previously shown the silent discharge and the short wave-length radiations of sparks to possess both ozonizing and deozonizing properties and Regener⁷ had shown that the deozonizing effect is produced by wave-lengths absorbed by glass but not by quartz. Regener found that a concentration of 2.2 per cent ozone could be produced by irradiating oxygen with the light from an aluminum spark, the chief intensity of which lies between 1719 and 1884Å. The same stationary concentration was also produced when a gas containing a concentration of 6 per cent of ozone (prepared by the action of a silent discharge) was irradiated by the spark. The scant absorption data then available indicated that the ozone was chiefly formed by radiations of 2000Å or less and that it was decomposed by wave-lengths between 2000 and 3000Å.

Chapman, Chadwick and Ramsbottom⁸ obtained considerable yields of ozone by the action of ultraviolet rays on partially dried oxygen, using a manometric method for following the reaction. At about this period several patents were

¹ Schönbein, C., *J. prakt. Chem.*, **75**, 99 (1858).

² Nernst, W., *Jahresber. Elektr. Ges.*, **38** (1894), cited by Plotnikow, J., "Allgem. Photochemie," de Gruyter, Berlin, 1936, 565.

³ Lenard, P., *Ann. Physik*, **1**, 486 (1900).

⁴ Goldstein, E., *Ber.*, **36**, 3042 (1903).

⁵ Fischer, F., and Braehmer, F., *Ber.*, **38**, 2633 (1905).

⁶ Warburg, E., and Regener, E., *Sitzber. K. Akad. Wiss. Berlin*, 1228, 1904; *J. Chem. Soc.*, **86**, (ii), 692 (1904).

⁷ Regener, E., *Ann. Physik*, **20**, 1033 (1906). For a recent theoretical discussion of the equilibrium between ozone formation and decomposition, see Eucken, A., and Patat, F., *Z. physik. Chem.*, **33B**, 459 (1936).

granted for the production of ozone in various types of apparatus by the action of ultraviolet radiations.⁹

The formation of ozone in the vicinity of quartz mercury arcs is now a familiar observation. Dadlez¹⁰ measured the diminution of the ozone content of the air at increasing distances from lamps of various makers to determine whether ozone is formed in sufficient amount to constitute a health hazard to operators of these lamps. He found that concentrations not greater than 0.05-0.3 mg. per cubic meter are produced under favorable conditions. Symptoms of distress are produced only when the concentration reaches 1.0 to 1.5 mg. per cubic meter and 4 mg. per cubic meter are necessary to render the atmosphere unsupportable to life. Nevertheless, Cornelius¹¹ recommended filtration to eliminate the rays forming ozone, at least in drying patent leather.

The formation of ozone by the shortest wave-lengths of the mercury arc, chiefly the 1850A line, may be now considered in the light of early work on the band spectra of oxygen. A series of bands in the Schumann region observed and measured by Schumann¹² and by Runge¹³ are known as the Schumann-Runge bands. They begin at about 1925 to 2026A according to Leifson,¹⁴ and converge to a limit at 1751A.¹⁵ Detailed term analyses of these bands have been given by Ossenbrüggen.¹⁶ Flory¹⁷ believes the O₂ molecule predissociates in the band region above 1751A into normal ³P atoms. Quantitative absorption data by Ladenburg, Van Voorhis and Boyce¹⁸ and by Granath¹⁹ indicate that the limit is followed by a region of continuous absorption which has its maximum at 1450A, and continues to nearly 1300A.²⁰ It has been subsequently shown that the products of the dissociation which occurs at or beyond 1751A are a normal ³P and an excited ¹D oxygen atom.²¹ Frerichs²² found the excitation energy of the ¹D oxygen atom to be 1.06 e-volt. When this energy is deducted from that which corresponds to the convergence limit (7.05 volts), the heat of dissociation of oxygen into two normal atoms is found to be 5.09 e-volts, which corresponds to 117.3 kcal. or 2429A. Data on the kinetics of the reaction produced by the mercury line at 1850A are not available. Working with radiations of wave-lengths 1862 to 1719A, Eucken²³ found a negative temperature coefficient for the conversion of oxygen at very low pressures into ozone at temperatures between those of the room and liquid air.

⁹ Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 947 (1907); see also Bordier, H., and Nogier, T., *Compt. rend.*, **147**, 354 (1908) and v. Aubel, E., *Ibid.*, **149**, 983 (1909); **150**, 96 (1910).

¹⁰ Potter, H. N., U. S. P. 854,965 May 28, 1907; Jaubert, G. F., French P. 415,574, July 19, 1909; Davis, N. W., U. S. P. 1,209,132, Dec. 19, 1916; *Chem. Abs.*, **11**, 549 (1917).

¹¹ Dadlez, J., *Compt. rend.*, **185**, 89 (1927); *L'Union Pharm.*, **69**, 17 (1928); *Chem. Abs.*, **23**, 2660 (1929).

¹² Cornelius, F., *Chim. et Ind.*, **6**, 218 (1921); German P. 318,065, Nov. 15, 1916.

¹³ Schumann, V., *Smithsonian Contributions to Knowledge*, **29**, No. 1413 (1903).

¹⁴ Runge, C., *Physica*, **1**, 254 (1921).

¹⁵ Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926); Hopfield, J. J., and Leifson, S. W., *Phys. Rev.*, **25**, 716 (1925).

¹⁶ Birge, R. T., and Spomer, H., *Phys. Rev.*, **28**, 259, 270 (1926).

¹⁷ Ossenbrüggen, W., *Z. Physik*, **49**, 167 (1928).

¹⁸ Flory, P. J., *J. Chem. Physics*, **4**, 23 (1936).

¹⁹ Ladenburg, R., Van Voorhis, C. C., and Boyce, J. C., *Phys. Rev.*, **40**, 1018 (1932); Ladenburg has also reviewed the work on absorption by atmospheric oxygen. *J. Opt. Soc. Am.*, **25**, 259 (1935).

²⁰ Granath, L. P., *Phys. Rev.*, **34**, 1046 (1929).

²¹ Stueckelberg, E. C. G., *Phys. Rev.*, **42**, 518 (1932).

²² Herzberg, G., *Z. physik. Chem.*, **4B**, 223 (1929).

²³ Frerichs, R., *Phys. Rev.*, **36**, 398 (1930).

²⁴ Eucken, A., *Z. physik. Chem.*, **107**, 436 (1923).

The absorption data thus far considered are not adequate to explain the results of Warburg on the formation of ozone by the irradiation of oxygen in a streaming system with the lines 2070 and 2530A.²⁴ These wave-lengths are longer than the Schumann-Runge bands and in order to secure sufficient absorption for a reaction to occur, it was necessary to employ the oxygen at high pressures. With the wave-length 2070A, Warburg found a quantum yield of 3.1 when the oxygen pressure was 125 kg. per square cm., and somewhat lower values at pressures as high as 300 kg. With the longer wave-length, 2530A, the quantum yields were somewhat lower and the same drop was observed with increase in pressure. Warburg attributed the decrease in yield with increase in pressure to some influence of adjacent molecules upon each other which affected their ability to absorb radiations. The absorption of the 2070A line was found to increase nearly seven times when the pressure was raised from about 30 to 325 kg. per square cm.²⁵ Noyes,²⁶ who has given a critical historical discussion of the reaction, believes, however, that the observed pressure effect on the quantum yield was not much greater than the possible experimental errors.

To account for the quantum yield of three, Warburg suggested, in the case of the 2070A line, a primary dissociation into atoms. This, however, is in disagreement with the subsequent findings upon the convergence limit of the Schumann-Runge bands. Warburg recognized that the 2530A line could not produce a dissociation of oxygen and suggested that a mechanism involving excited molecules would be necessary.

Further interpretations of the results of Warburg have been given by Wulf,²⁷ who has pointed out that the oxygen molecule does not absorb in the regions Warburg found effective. Certain weak bands which have been found in long paths of oxygen at ordinary pressures²⁸ and in compressed or liquid oxygen²⁹ appear to converge to a limit at 2429A. This agrees with the energy required for the dissociation of oxygen into normal atoms. The weak bands are followed by a weak continuous region which extends to shorter wave-lengths and even underlies the Schumann-Runge bands. Wulf believes that the light of wave-length 2070A, in Warburg's experiments was absorbed by this continuum. He ascribes the new bands, at least in part, to a van der Waals molecule, O₄, the presence of which in highly compressed oxygen had previously been suggested by Lewis³⁰ from a consideration of the magnetic susceptibility of oxygen at low temperatures. In support of this, Wulf cites the fact that the absorption intensity at 2470A increases as the square of the oxygen pressure. From an extrapolation of data of Liveing and Dewar,³¹ he computed the region of the beginning of the continuous spectrum following the bands to be near 2470A, which he thought might correspond to dissociation into an ozone molecule and an oxygen atom. Guillien³² also interprets data on the absorption of liquid oxygen as indicative of an equilibrium between O₂ and O₄ molecules. A set of bands lying in the region of the con-

²⁴ Warburg, E., *Sitzb. Akad. Wiss.*, 216 (1912); 872 (1914); *Z. Elektrochem.*, 27, 133 (1921).

²⁵ Warburg, E., *Sitzb. Akad. Wiss. Berlin*, 230, 1915; *J. Chem. Soc.*, 118 (ii), 404 (1920).

²⁶ Noyes, W. A., Jr., *Rev. Modern Physics*, 5, 283 (1933).

²⁷ Wulf, O. R., *Proc. Nat. Acad. Sci.*, 4, 356 (1928); 14, 609 (1928); *J. Opt. Soc. Am.*, 25, 231 (1935).

²⁸ Herzberg, G., *Naturwiss.*, 20, 577 (1932).

²⁹ Ciechowski, L., *Beibl. Ann. Physik*, 39, 240 (1915); Shaver, W. W., *Proc. Roy. Soc. Canada*, 15, (III), 7 (1921). For the absorption of solid oxygen, see Prikhot'ko, A., Ruhemann, M., and Federitkenko, A., *Physik. Z. Sowjetunion*, 7, 410 (1935); *Chem. Abs.*, 29, 6141 (1935).

³⁰ Lewis, G. N., *J. Am. Chem. Soc.*, 46, 2027 (1924).

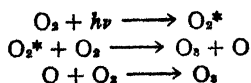
³¹ Liveing, G. D., and Dewar, Sir J., *Proc. Roy. Soc.*, 46, 222 (1889).

³² Guillien, R., *Compt. rend.*, 198, 1486 (1934).

vergence of the Herzberg bands has been found by Finkelnburg and Steiner³³ to vary in intensity with the square of the pressure, although they attributed the effect to the proximity of two oxygen molecules rather than to the formation of O_4 .³⁴ The arguments for and against polymerization have been critically discussed by Wulf.³⁵ A final conclusion between the possibility of the existence of O_4 and absorption by a pair of O_2 molecules during collision has not been reached. Steiner³⁶ does not believe the oxygen molecule should be considered a free radical, despite its paramagnetism, since the spin interaction between two oxygen molecules has a very low energy, not of the order of magnitude involved in chemical reaction.

It has been claimed by Dickinson and Sherill³⁷ that the formation of ozone at atmospheric pressure can be stimulated by the presence of excited mercury atoms. Collision of an oxygen molecule with an excited mercury atom can give it nearly the energy necessary for dissociation into normal atoms^{37a} or the excited mercury atom may on collision produce an excited oxygen molecule.

Radiations passing through fluorite (average wave-length 1750A and therefore close to or shorter than the convergence limit of the Schumann-Runge bands) form ozone in oxygen at atmospheric pressure with a quantum efficiency of two.³⁸ In the region of the bands the primary process has been believed to be the formation of an excited molecule followed by reactions as indicated in the scheme:



The latter two processes are assumed to occur on the walls or as a result of triple collisions. In the region of continuous absorption, two oxygen atoms, one excited (1D) are produced, and each then is assumed to combine with an oxygen molecule. If, as Flory suggests, the primary process is one of predissociation, the first equation would yield oxygen atoms directly, eliminating the necessity for the second equation.

The Decomposition of Ozone. Ozone possesses absorption bands both in the visible and in the ultraviolet regions and decomposition can be effected by absorption of light in either of these regions. Although the first investigations were conducted in the ultraviolet range, it is simplest to begin with the effects of visible light.

Ladenburg and Lehmann³⁹ showed ozone to possess a group of visible absorption bands,⁴⁰ for which Colange⁴¹ has given quantitative absorption data. The diffuseness of the bands indicates the occurrence of predissociation.

³³ Finkelnburg, W., and Steiner, W., *Z. Physik*, **79**, 69 (1932).

³⁴ See also Steiner, W., *Trans. Faraday Soc.*, **30**, 34 (1934) and Salow, H., and Steiner, W., *Z. Physik*, **99**, 137 (1936).

³⁵ Wulf, O. R., *J. Am. Chem. Soc.*, **50**, 2596 (1928).

³⁶ Salow, H., and Steiner, W., *Nature*, **134**, 463 (1934).

³⁷ Dickinson, R. G., and Sherill, M. S., *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); for a detailed discussion see Franck, J., *J. Phys. Chem. U.S.S.R.*, **5**, 1013 (1934).

^{37a} Presumably the deficit is made up thermally.

³⁸ Vaughan, W. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **52**, 559 (1930); Groth, W. [*Z. physik. Chem.*, **37B**, 307 (1937)] finds it 1.90 for the xenon lines 1295 and 1470A.

³⁹ Ladenburg, R., and Lehmann, E., *Ann. Physik*, **21**, 305 (1906).

⁴⁰ See also Wulf, O. R., *Proc. Nat. Acad. Sci.*, **16**, 508 (1930).

⁴¹ Colange, G., *J. Phys. Radium*, **8**, 254 (1927).

⁴² Griffith R. O., and Shutt, W. J., *J. Chem. Soc.*, **119**, 1948 (1921); **123**, 2752 (1923).

By the use of filters, Griffith and Shutt⁴² concluded the most effective spectral regions to lie between 7600 and 6700Å and between 6150 and 5100Å. The decomposition rate was proportional to the square of the ozone concentration. They believed the reaction to be catalyzed by hydrogen. Some water formation was also observed in accordance with the reaction $H_2 + O_3 \rightarrow H_2O + O_2$. This latter reaction became predominant when the original ozone concentration was below 2.4 per cent. In the presence of carbon monoxide,⁴³ some carbon dioxide was produced in an analogous reaction, which, however, occurred to but a slight extent. The simple ozone decomposition was said to be catalyzed by foreign gases in the following decreasing order of effectiveness: hydrogen, (far more effective than the others), helium, argon, nitrogen, carbon monoxide, and carbon dioxide. These authors believed the mechanism of the decomposition to involve the formation of activated molecules of ozone. These were then thought to combine each with an ozone molecule in its ground state to form a complex which, on collision with other molecules, might dissociate to yield from each complex three oxygen molecules. The temperature coefficient of the reaction was found to increase with the wave-length.

Similar results were reported by Kistiakowsky,⁴⁴ who employed monochromatic light of 6200Å, used mixtures containing up to 70 per cent of ozone and varied the total gas pressures from atmospheric down to 9 mm. He found the quantum yields to be greater than two, and a direct function of the amount of red light absorbed and of the effective pressure of ozone in the system. He believed that in the absence of other added gases oxygen acted as an effective deactivator of excited ozone molecules and that those gases which, like hydrogen, seemed to catalyze the decomposition, appeared to do so only because they were less effective inhibitors than oxygen.

Schumacher⁴⁵ proposed a mechanism involving a photodissociation of the ozone into an oxygen molecule and an oxygen atom. Visible light is energetically capable of effecting this process, which requires 24.6 kcal., although this was not known at the time of Kistiakowsky's first paper. The foreign gas inhibitions were attributed to their specific effects on the recombination of the dissociation products to form ozone in three-body collisions. In the case of hydrogen, an interaction of the oxygen atom with the hydrogen molecules to form water was suggested as the cause of the ten-fold increase in the velocity of the ozone decomposition.

The strong absorption of ozone in the ultraviolet region has been the subject of numerous investigations, some of which have been discussed in Chapter 10. The maximum lies at about 2550Å. According to Wulf and Melvin,⁴⁶ the spectrum appears partly banded and partly continuous; the bands, of which there are 23 of weak intensity between 3050 and 3400Å, become sharper at low temperatures. Schumacher⁴⁷ believes an underlying continuum may be due to dissociation into an oxygen molecule in the ground state and an excited oxygen atom, or *vice versa*. Kondratjew⁴⁸ suggests that at wave-lengths less than 2700Å both dissociation

⁴² Griffith, R. O., and McWillie, J., *J. Chem. Soc.*, 123, 2767 (1923); Griffith, R. O., and McKeown, A., *Trans. Faraday Soc.*, 21, 597 (1926).

⁴³ Kistiakowsky, G. B., *Z. physik. Chem.*, 117, 337 (1925).

⁴⁴ Schumacher, H. J., *J. Am. Chem. Soc.*, 52, 2377 (1930); Schumacher, H. J., and Sprenger, G., *Z. physik. Chem.*, 11B, 38 (1930); *Z. Elektrochem.*, 38, 620 (1932).

⁴⁵ Wulf, O. R., and Melvin, E. H., *Phys. Rev.*, 38, 333 (1930).

⁴⁶ Schumacher, H. J., *J. Am. Chem. Soc.*, 52, 2389 (1930).

⁴⁷ Kondratjew, V., *Z. physik. Chem.*, 7B, 70 (1930); Jakolewa, A., and Kondratjew, V., *Physik. Z. Sowjetunion*, 1, 472 (1932).

products may be in excited states. Mecke,⁴⁹ admits this possibility but places the wave-length limit at 2655A.⁵⁰

Early observations upon the rate of the decomposition of ozone in ultraviolet light were reported by v. Bahr⁵¹ and by Weigert.⁵² In the presence of hydrogen, a catalysis was observed.

Using the wave-length 2530A, Warburg⁵³ measured the quantum yield of the reaction under various conditions. For low concentrations of ozone, about 0.5 per cent or less, the yield was 0.28. It was considerably greater in the presence of nitrogen (1.1) or helium (1.7). For high ozone concentrations, the yields increased to 3.5 at 9 per cent. With moist ozone at about this concentration, the use of the wave-length 2090A gave a quantum yield as high as 8, suggesting a chain reaction.

Schumacher and Beretta⁵⁴ find the mechanism of the reaction due to the wave length 3130A to be similar to that occurring in red light. Heidt and Forbes⁵⁵ find from the magnitude of the quantum efficiency of the decomposition of pure, dry ozone that even in the absence of water vapor the reaction produced by 2080, 2540 or 2800A has chain characteristics. The yields were frequently above two, sometimes four and even as high as 6.7. The quantum efficiency increased with the partial pressure of ozone and decreased with that of oxygen. No dependence of the quantum yield upon the wave-length was observed. The temperature coefficient was 1.2, or possibly slightly greater at very low temperatures. Heidt⁵⁶ later found approximately the same quantum yields at 3130A as at 2080A.

The Chlorine-Sensitized Decomposition of Ozone. In regions in which ozone does not absorb, its decomposition can be brought about by the addition of chlorine as a photosensitizer. This reaction was discovered by Weigert,⁵⁷ who concluded its rate to be proportional to the light absorbed by the chlorine and independent of the ozone concentration. Bonhoeffer⁵⁸ found the absorption of one quantum (4360 or 4050A) to produce the decomposition of two molecules of ozone. More recent observations by Allmand and Spinks⁵⁹ have shown quantum yields as high as 30 (in some cases 59) at high ozone concentrations. Under these conditions the rate of reaction is proportional to the square root of the light intensity. Schumacher and Wagner⁶⁰ suggested the formation of ClO as an intermediate product in this reaction, and Bodenstein, Harteck and Padelt⁶¹ gave evidence for the formation of some ClO₃. There are many complicating features, as an induction period (not observed by Weigert) and after effects. Allmand and Spinks suggested that

⁴⁹ Mecke, R., *Z. physik. Chem. Bodenstein Festband*, 392 (1931).

⁵⁰ For further details on the absorption spectrum of ozone in the ultraviolet, see Lauchli, A., *Helv. phys. Acta*, 1, 232 (1928); *Z. Physik*, 53, 92 (1929); Duthell, J. and M., *J. Phys. Radium*, 7, 415 (1926); Cabannes, J., and Dufay, J., *J. Phys. Radium*, 7, 257 (1926); Chalonge, D., and Lambrey, M., *Compt. rend.*, 184, 1165 (1927); Tsi-Zé, N., and Shin-Piaw, C., *Compt. rend.*, 195, 309 (1932); Vassy, E., *Compt. rend.*, 202, 1426 (1936).

⁵¹ v. Bahr, E., *Ann. Physik*, 33, 598 (1910).

⁵² Weigert, F., *Z. physik. Chem.*, 80, 78 (1912); *Ber.*, 46, 815 (1913); Weigert, F., and Böhm, H., *Z. physik. Chem.*, 90, 189 (1915).

⁵³ Warburg, E., *Sitzb. Preuss. Akad.*, 644 (1913).

⁵⁴ Schumacher, H. J., and Beretta, U., *Z. physik. Chem.*, 17B, 405, 417 (1932); Ritchie, M., *Proc. Roy. Soc.*, 146A, 848 (1934).

⁵⁵ Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.*, 56, 2365 (1934).

⁵⁶ Heidt, L. J., *J. Am. Chem. Soc.*, 57, 1710 (1935).

⁵⁷ Weigert, F., *Ann. Physik*, 24, 243 (1907); *Z. Elektrochem.*, 14, 591 (1908).

⁵⁸ Bonhoeffer, K. F., *Z. Physik*, 13, 94 (1923).

⁵⁹ Allmand, A. J., and Spinks, J. W. T., *Nature*, 124, 651 (1929); *J. Chem. Soc.*, 1652 (1931); 599 (1932).

⁶⁰ Schumacher, H. J., and Wagner, C., *Z. physik. Chem.*, 5B, 199 (1929).

⁶¹ Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.*, 147, 233 (1925).

chlorine atoms, formed in the primary absorption process, may combine to ClO_3 on collision with ozone molecules and that a chain reaction may ensue and be terminated by the absorption of intermediate atoms or groups on the walls. Furthermore, some ClO_3 molecules may unite to form chlorine hexoxide which in the presence of water forms chloric and perchloric acids. The combination of Cl atoms and oxygen molecules may also give rise to ClO_2 . The latter, reacting with ozone, forms oxygen molecules and ClO_3 groups.

Heidt, Kistiakowsky and Forbes⁶² found highly abnormal temperature coefficients ranging from 0.7 to 14.6. The purer the gases the more erratic were the results and the more prominent a "fast" reaction in the dark following a brief exposure to light. A marked decrease in the rate with the time of illumination was also observed. No mechanism could be proposed capable of explaining the results. In a subsequent investigation, Norrish and Neville⁶³ observed a red liquid oxide of chlorine $(\text{ClO}_3)_n$ and suggested that its separation and slow decomposition might in some manner account for the observations of Heidt, Kistiakowsky and Forbes. Norrish and Neville found that at low ozone concentrations, the reaction is of zero order and has a chain mechanism. At high ozone concentrations, in agreement with Allmand and Spinks, the rate was proportional to the square root of the light intensity (3650Å). At high concentrations of oxygen and chlorine, the rate was proportional to the first power of the intensity and the reaction was inhibited. The quantum yields varied from two to about ten. Chains may be propagated both by chlorine atoms and by ClO radicals. Nitrogen and carbon dioxide appeared to have no effect on the reaction. Rollefson and Byrns⁶⁴ isolated ClO_3 from the reaction mixture and noted that its occurrence therein prevents pressure measurements from affording an accurate indication of the amount of ozone decomposed. They also produced evidence for a reaction mechanism involving Cl_2O_7 .

The chlorine-sensitized decomposition of ozone was used in actinometry by Cremer⁶⁵ since when low ozone concentrations are employed and light absorbed only by chlorine is used, the quantum yield is generally found to be two. Even in carbon tetrachloride solution, quantum yields of two have been observed for both the unsensitized and the sensitized ozone decompositions.⁶⁶

The effect of irradiation of ozone-chlorine mixtures by wave-lengths absorbed by the ozone rather than by the chlorine has been investigated by Bodenstein and Schumacher,⁶⁷ who proposed a mechanism involving directly excited ozone molecules. These were thought to react with chlorine molecules with the formation of the ClO radical and ClO_2 . They found also that chlorine hexoxide was produced and that its yield could be increased by lowering the temperature or by increasing the size of the reaction vessel.

THE FORMATION AND DECOMPOSITION OF WATER

Absorption. Water vapor commences to absorb light quite suddenly at about 1800Å.⁶⁸ Rathenau⁶⁹ found predissociation bands between 1780 and 1540Å and

⁶² Heidt, L. J., Kistiakowsky, G. B., and Forbes, G. S., *J. Am. Chem. Soc.*, **55**, 223 (1933).

⁶³ Norrish, R. G. W., and Neville, G. H. J., *Nature*, **131**, 544 (1933); *J. Chem. Soc.*, 1864 (1934).

⁶⁴ Rollefson, G. K., and Byrns, A. C., *J. Am. Chem. Soc.*, **56**, 364 (1934).

⁶⁵ Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

⁶⁶ Bowen, E. J., Moelwyn-Hughes, E. A., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **134A**, 211 (1931).

⁶⁷ Bodenstein, M., and Schumacher, H. J., *Z. physik. Chem.*, **53B**, 233 (1929).

⁶⁸ [1830Å in 17 mm. layers of liquid water, Kreusler, H., *Ann. Physik*, **6**, 412 (1901)]; Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27**, 193 (1931).

⁶⁹ Rathenau, G., *Z. Physik*, **87**, 32 (1933).

again at 1340Å. Mecke⁷⁰ believes there is a series of bands converging at 1390Å, corresponding to a dissociation into an excited hydroxyl radical and a hydrogen atom. A continuous region near 1800Å may correspond to a dissociation into a hydrogen atom and a normal state hydroxyl radical. Quantitative data on the absorption of water in the longer wave-length ultraviolet and in the visible have been given by Granath⁷¹ and by Dawson and Hulburt.⁷²

According to Plotnikow, the first observation of the photo-chemical decomposition of water into hydrogen and oxygen was made by Baker.⁷³ Similar observations were made by early workers with the quartz mercury arc.⁷⁴ Tian,⁷⁵ who obtained traces of hydrogen peroxide, clearly recognized that only the shortest waves passing through quartz were capable of effecting the decomposition of water. Dhar⁷⁶ believes water vapor in the upper atmosphere to be decomposed by the solar ultraviolet.

Coehn⁷⁷ described the production of a stationary state in which irradiation of water vapor caused a decomposition of 0.2 per cent; the decomposition increased with the light intensity and decreasing pressure. Andrejeff,⁷⁸ however, found that at 200°C., in the stationary state, decomposition had proceeded to only 0.002 per cent. No theoretical studies from the modern viewpoint are available.

The formation of hydrogen peroxide from water and oxygen by ultraviolet rays has been observed. It appeared to depend largely upon special experimental conditions or possibly upon the presence of impurities.⁷⁹

Earlier workers claimed to have been able to induce the combination of hydrogen and oxygen by exposure to the ultraviolet radiations of a mercury arc. Although Thiele⁸⁰ believed the presence of moisture not to be necessary for the combination to occur, Baker and Carlton⁸¹ were unable to observe any contraction during irradiation for five or six hours of gases which had been dried several weeks. Wet gases showed a certain amount of reaction during the same period of irradiation.

Kistiakowsky⁸² investigated the reaction in two wave-length regions, the source being a condensed spark between aluminum disk electrodes. When the lines about 1720Å, that is, within the continuous absorption region of oxygen, were employed, the yield of ozone in the presence of hydrogen was only one-fourth of that in the presence of nitrogen and an equal amount of hydrogen peroxide was also formed. The ozone yields were proportional to the relative concentrations of oxygen in the hydrogen-oxygen mixture, and the yields of hydrogen peroxide were proportional to the concentration of hydrogen. In the more recent experiments it was found that in the presence of increasing concentrations of hydrogen, the ozone yield decreased to zero and the yield of hydrogen peroxide increased. At

⁷⁰ Mecke, R., *Trans. Faraday Soc.*, **27**, 369 (1931).

⁷¹ Granath, L. P., *Phys. Rev.*, **34**, 1046 (1929).

⁷² Dawson, L. H., and Hulburt, E. O., *J. Opt. Soc. Am.*, **24**, 175 (1934).

⁷³ Baker, H. B., *Proc. Chem. Soc.*, **18**, 40 (1902).

⁷⁴ Fischer, F., and Braehmer, F., *Ber.*, **79**, 958 (1906); Thiele, H., *Ber.*, **40**, 4914 (1907); *Z. angew. Chem.*, **22**, 2472 (1909); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1191 (1910); **152**, 522 (1911); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910).

⁷⁵ Tian, A., *Compt. rend.*, **152**, 1483 (1911); **151**, 1040 (1911).

⁷⁶ Dhar, N. R., *Trans. Faraday Soc.*, **30**, 142 (1934).

⁷⁷ Coehn, A., *Ber.*, **43**, 880 (1910).

⁷⁸ Andrejeff, I., *Z. Elektrochem.*, **19**, 551 (1913).

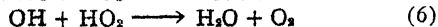
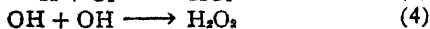
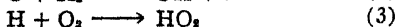
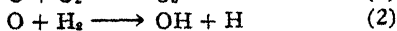
⁷⁹ Kernbaum, M., *Compt. rend.*, **148**, 705 (1909); **149**, 116, 273 (1909).

⁸⁰ Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).

⁸¹ Baker, H. B., and Carlton, M., *J. Soc. Chem. Ind.*, **44**, 1047 (1925).

⁸² Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **52**, 1868 (1930); Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

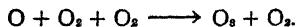
high pressures, the yield of water parallels that of hydrogen peroxide. At lower pressures, the yield of water also increases, although not at the expense of ozone or peroxide. In a one to one oxygen-hydrogen mixture, the rates at which the excited oxygen atoms react with oxygen or hydrogen are nearly equal. The following system of partial reactions was suggested:



It was believed that (2) did not occur readily, the hydrogen molecule showing an unexpected stability. However, the possibility that oxygen atoms might unite with hydrogen in three-body collisions with oxygen molecules appeared to be admissible, (2) and (3) occurring together as



Kistiakowsky and Smith believed, contrary to Ritchie,⁸³ that reaction (1) has an activation energy of zero. Nevertheless, the formation of ozone was also thought to take place in triple collisions



In later experiments (1935) it was possible to demonstrate the formation of hydrogen peroxide which had been missed in the earlier experiments (1930), even when wave-lengths of the band region (1854-1862Å) were alone employed, the strong aluminum lines at 1720Å being removed by an oxygen filter. The yield, however, was only half that produced in the experiments with shorter wave-lengths. It appeared that one-half of the absorbed light of the longer wave-lengths forms ozone irrespective of the composition of the gases, the other half giving rise to the same sequence of reactions as occur under shorter wave-length illumination. To explain this, the primary process was assumed to be the formation of excited oxygen molecules which react with oxygen molecules⁸⁴ to give ozone and atomic oxygen, but which suffer only elastic collisions with hydrogen. No attempt was made to determine the rate of water formation in this region.

Flory⁸⁵ suggests that in the band region predissociation of oxygen produces two normal state oxygen atoms, and that the differences in the reaction as conducted in the band and continuous regions are to be attributed to the different states of the oxygen atoms formed by predissociation and by dissociation.

Neufmin and Popov⁸⁶ also studied the reaction in the Schumann region, using hydrogen at 0.1 mm. pressure, and found quantum yields (for peroxide formation) of approximately 0.1. Their mechanism was similar to that subsequently given by Kistiakowsky, except that they believed that in the reaction between excited oxygen atoms and hydrogen molecules, the hydroxyl radical formed (along with a

⁸³ Ritchie, M., *Proc. Roy. Soc.*, **146A**, 848 (1934).

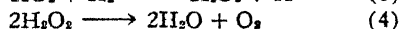
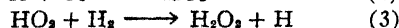
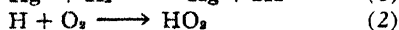
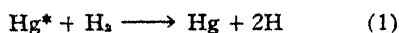
⁸⁴ See also Klemenc, A., and Patat, F., *Naturwiss.*, **18**, 281 (1930).

⁸⁵ Flory, P. J., *J. Chem. Physics*, **4**, 23 (1936).

⁸⁶ Neufmin, H., and Popov, B., *Z. physik. Chem.*, **27B**, 15 (1934). For more recent studies with the xenon lamp, see W. Groth and P. Hartek, *Z. Elektrochem.*, **44**, 621 (1938).

hydrogen atom) was excited with vibrational energy up to 2 electron-volts. They also assumed that the combination of two hydroxyl radicals was a wall reaction. Miyanishi⁸⁷ studied the influence of temperature upon the reaction. Kistiakowsky found the formation of water to be greatly increased at high temperatures.

The Mercury-Sensitized Reaction. (See also page 257, chapter 16.) Marshall⁸⁸ investigated the mercury-sensitized reaction of hydrogen and oxygen. At 50°C., the fall in pressure of dried gas mixtures ranging in composition from 406 mm. hydrogen and 148 mm. oxygen to 572 mm. hydrogen and 156 mm. oxygen, was 24.7 mm. per minute. The pressure-time curves showed an initial break at a point corresponding with saturation of the gas with water-vapor, after which the curves were linear. When oxygen was present in excess, the rate decreased rapidly as the reaction proceeded. However, in the reaction of stoichiometric mixtures, the rate remained constant. Marshall believed the true temperature coefficient to be near unity, but experimentally many corrections were necessary because the concentration of mercury vapor varied with the temperature and because the quantum yield varied with temperature. For the formation of hydrogen peroxide, the quantum yield was found to be 2.5.^{88a} At least 75 per cent of the total yield of products was peroxide. The mechanism suggested involved the reactions,



Marshall⁸⁹ later found the optimum mercury vapor pressure for the formation of hydrogen peroxide to be 0.005 mm. The greater rate of reaction in the presence of higher concentrations of mercury was offset by decomposition of the hydrogen peroxide formed. The rate of the reaction probably varied as the first power of the light intensity. The maximum rate of formation of hydrogen peroxide was 2 gm. per hour.

Frankenburger and Klinkhardt,⁹⁰ obtained somewhat different quantum yields at room temperature. The quantum yield for water was greater (1.5-2.5) and that for hydrogen peroxide lower (1-2). They objected to the mechanism proposed by Marshall for the formation of hydrogen peroxide (Reactions 2 and 3) on the ground that the reaction $\text{HO}_2 + \text{H}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{H}$ is endothermic by 31 kcal. Barak and Taylor reported that this conclusion was based upon an unwarranted assumption, and stated that reactions 2 and 3 are together exothermic. Farkas and Sachsse⁹¹ have shown that hydrogen atoms react with O_2 molecules to produce HO_2 by three-body collisions. It is necessary to build up a mechanism of the type devised by Marshall if the quantum yield of hydrogen peroxide is really two or greater, since a chain mechanism is demanded. If, however, as Frankenburger found, the yield is lower, a chain mechanism is not necessary. Then, however, it would be necessary to account for the higher yields of water, assumed to be formed

⁸⁷ Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **26**, 70 (1935); *Chem. Abs.*, **29**, 2852 (1935).

⁸⁸ Marshall, A. L., *J. Phys. Chem.*, **30**, 34, 1078 (1926); Taylor, H. S., and Marshall, A. L., *Ibid.*, **29**, 842, 1140 (1925).

^{88a} This represented a correction of an earlier value of 6.6, in error because of the use of an incorrect value for the transmission of the filter.

⁸⁹ Marshall, A. L., *J. Am. Chem. Soc.*, **49**, 2763 (1927).

⁹⁰ Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc.*, **27**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932); see also Barak, M., and Taylor, H. S., *Trans. Faraday Soc.*, **28**, 569 (1932).

⁹¹ Farkas, L., and Sachsse, H., *Z. physik. Chem.*, **27B**, 111 (1934).

directly and not through hydrogen peroxide, by a chain mechanism, as one proposed by Bonhoeffer and Haber.⁹² Frankenburger and Klinkhardt assumed the hydrogen peroxide to be formed by the union of two OH radicals in a three-body collision. Bates⁹³ suggested that the discrepancy between the results of Frankenburger and Klinkhardt and those of Marshall may be due to the fact that the former workers used a light intensity a hundred-fold greater than that employed by Marshall. Bates favored the Marshall mechanism.

The amount of mercuric oxide formed in the course of the reaction may exert a considerable effect upon the rate and may influence the results. Noyes⁹⁴ found no appreciable reaction between mercury and normal state oxygen atoms. But under conditions in which ozone may be formed, there is a reaction. Noyes also suggested the possibility of the formation of a relatively unstable complex (between excited mercury atoms and oxygen) which may be converted into ozone on collision with oxygen molecules. Franck⁹⁵ finds that at pressures of oxygen below 1 cm., the formation of mercuric oxide initiated by excited mercury atoms is proportional to the incident intensity of the resonance line of mercury and to the number of damped collisions of mercury with oxygen. Also, the formation of the oxide was said to be independent of the presence of shorter wave-lengths in the incident radiation. At greater oxygen pressures, mercury oxide is formed when oxygen molecules alone are excited by the lines 1860, 1935 and 1990 Å, which produce ozone. Therefore, excited mercury is not necessary for the synthesis of mercuric oxide in the presence of ozone.⁹⁶

The velocity of the photosensitized reaction between hydrogen and oxygen is slightly higher than that between deuterium and oxygen, but the temperature coefficients of the two reactions seem to be identical.⁹⁷

The formation of water may also be sensitized by substances other than mercury. The formation of water during the combination of hydrogen and chlorine may be regarded as a reaction in which chlorine is the photosensitizer. In this reaction, Cremer⁹⁸ found the rate of formation of water to be proportional to the chlorine concentration. He suggested that an excited chlorine atom could pass its excitation energy over to an oxygen molecule, as could an excited Cl₂ molecule. The excited oxygen molecules might then react to form water by the process: $O_2^* + 2H_2 \longrightarrow 2H_2O$. Norrish⁹⁹ doubted this mechanism, since he believed the low excitation energy of the metastable chlorine atom would be insufficient to activate the oxygen molecule sufficiently to enable the latter to react with hydrogen. He stated that the inhibiting effect of oxygen on the hydrogen-chlorine combination is due to the reaction of molecules of oxygen with hydrogen atoms of the chain to form OH radicals. The latter can combine at ordinary temperatures to hydrogen peroxide. He found the peroxide to be produced in appreciable quantities when mixtures of oxygen, hydrogen and chlorine at atmospheric pressure were irradiated with light from a mercury arc. Also, it

⁹² Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

⁹³ Bates, J. R., *J. Am. Chem. Soc.*, **55**, 426 (1933); *J. Chem. Physics*, **1**, 457 (1933).

⁹⁴ Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 3104 (1927); *Z. physik. Chem.*, **2B**, 445 (1929).

⁹⁵ Franck, J., *Compt. rend. Acad. Sci. U.R.S.S.*, **4**, 146 (1933); *Brit. Chem. Abs.*, **A**, 263 (1934); *Acta Physicochim. U.R.S.S.*, **1**, 833 (1934); *J. Phys. Chem. (U.S.S.R.)*, **5**, 1013 (1934); *Chem. Abs.*, **29**, 6507 (1935).

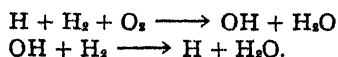
⁹⁶ It is also possible for the excited mercury atoms to produce some dissociation of water molecules, when and if present, into hydrogen atoms and normal state hydroxyl radicals. Sentfleben, H., and Rehren, I., *Z. Physik*, **37**, 529 (1926); Gaviola, E., *Temas de quim.*, **2**, 173 (1929); *Chem. Abs.*, **24**, 2376 (1930).

⁹⁷ Evans, M. G., *J. Chem. Physics*, **2**, 726 (1934).

⁹⁸ Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

⁹⁹ Norrish, R. G. W., *Trans. Faraday Soc.*, **27**, 461 (1931).

was stated¹⁰⁰ that if the partial pressure of chlorine in the mixture is above a certain critical value (temperatures between 0° and 300°C.) exposure of the mixture in glass to the light from a mercury vapor lamp will result in a practically instantaneous explosion with quantitative conversion of the hydrogen and oxygen to water. Below this partial pressure of chlorine, a rapid reaction between the hydrogen and chlorine occurs, only a trace of water being formed. The limiting pressure of chlorine increases rapidly as the lower temperatures are approached. His mechanism involved the reactions:



It was reported that the second of these reactions cannot occur spontaneously at temperatures below 400°C. In answering certain objections of Semenov,¹⁰¹ Norrish stated that for an explosion to occur, a small volume element of the mixture must become heated to 600°C.

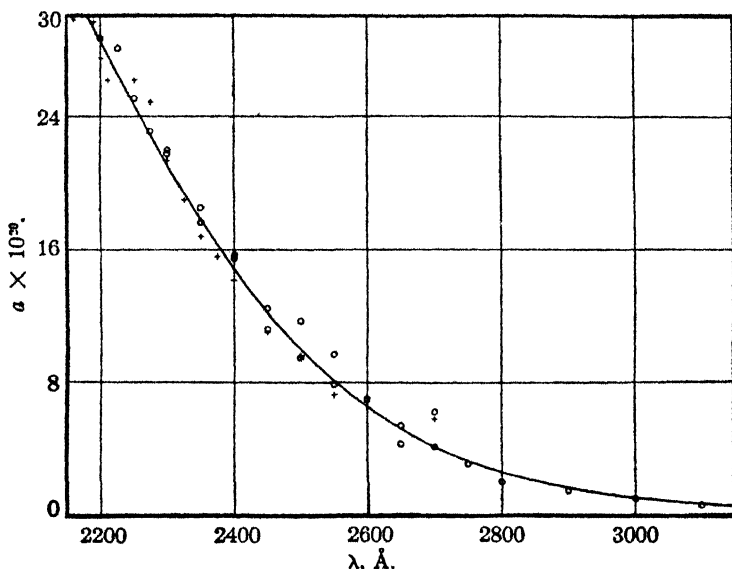


FIGURE 112. Absorption by Hydrogen Peroxide (Urey, Dawsey, and Rice, *Journal American Chemical Society*). + = vapor; o = solution.

Certain nitrogen compounds may also sensitize the reaction of hydrogen and oxygen. Farkas, Haber and Harteck¹⁰² found small quantities of ammonia to increase the reaction velocity at temperatures between 120°C. and 420°C. with and without irradiation by a zinc spark.¹⁰³ Taylor and Salley¹⁰⁴ measured the tem-

¹⁰⁰ Norrish, R. G. W., *Nature*, **127**, 853 (1931); *Proc. Roy. Soc.*, **135A**, 334 (1932); *Physik. Z. Sowj.*, **3**, 225 (1933).

¹⁰¹ Semenov, N., *Physik. Z. Sowj.*, **3**, 225 (1933).

¹⁰² Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **18**, 266 (1930).

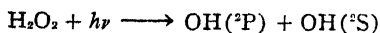
¹⁰³ See also Taylor, H. S., and Bates, J. R., *Nature*, **125**, 599 (1930) for the formation of atomic hydrogen by the photodissociation of ammonia.

¹⁰⁴ Taylor, H. S., and Salley, D. J., *J. Am. Chem. Soc.*, **55**, 96 (1933).

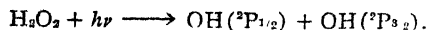
perature coefficients of the mercury-sensitized and of the ammonia-sensitized reactions at high temperatures. The results indicated that in the presence of ammonia long reaction chains occur above 300°C, but that in the mercury-sensitized reaction lengthening of the chains occurs only above 490°C. The chains may be propagated by atomic hydrogen, amino-radicals, or intermediate oxidation products.

Nitrogen peroxide functions also in photochemical combination of hydrogen and oxygen. On absorption of light the peroxide dissociates into NO and O which then start the reaction chain between hydrogen and oxygen.¹⁰⁵

The Decomposition of Hydrogen Peroxide. Urey, Dawsey and Rice¹⁰⁶ determined the coefficients of absorption of hydrogen peroxide vapor at room temperature (Figure 112). The continuous nature of the curve indicates a dissociation of the molecules. The peroxide molecule was regarded as formed of two OH radicals. From thermochemical data it did not appear possible to choose between the following methods of dissociation: (a) into 2OH, (b) into H and HO₂ and (c) into H₂O and O. The first possibility was favored since the emission spectrum of hydrogen peroxide, streamed rapidly through a cool discharge tube, was predominantly that of OH. Since illumination of hydrogen peroxide vapor with the zinc spark lines (2025-2138Å) caused the water bands (OH) to appear in fluorescence, it was concluded that the following reaction must occur:



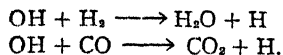
For wave-lengths between 2200 and 3000Å, there was favored the reaction



Sharma,¹⁰⁷ however, states that reduction of cupric oxide on irradiation in an absorption tube with hydrogen peroxide indicates the formation of atomic hydrogen (process b).

A mixture of 1 per cent hydrogen peroxide in carbon monoxide when circulated at 40° past a quartz window transmitting the wave-lengths 2070 and 2530Å produced carbon dioxide by a slow reaction.¹⁰⁸

When the carbon monoxide was replaced by hydrogen, water was formed. It was assumed that there was a primary decomposition of the peroxide into two hydroxyl radicals which then reacted slowly according to the mechanism proposed by Bonhoeffer and Haber¹⁰⁹ and by Lavin and Jackson.¹¹⁰



Had the photodissociation of the peroxide yielded instead water and an oxygen atom (process c), no interaction with hydrogen or carbon monoxide should have been observed, since the oxygen atoms would be expected to react much faster with hydrogen peroxide than with hydrogen or carbon monoxide. The reaction

¹⁰⁵ Norrish, R. G. W., and Griffiths, J. G. A., *Proc. Roy. Soc.*, **139A**, 147 (1933); Miyazishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **21**, 47 (1935); *Chem. Abs.*, **29**, 5351 (1935).

¹⁰⁶ Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929). See also Fergusson, W. C., Slotin, L., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 956 (1936).

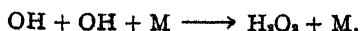
¹⁰⁷ Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

¹⁰⁸ v. Elbe, G., *J. Am. Chem. Soc.*, **54**, 822 (1932); **55**, 62 (1933).

¹⁰⁹ Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

¹¹⁰ Lavin, G. I., and Jackson, W. F., *J. Am. Chem. Soc.*, **53**, 383, 3189 (1931).

between OH and H_2 was considered to require an activation energy of not less than 14 kcal. This would keep the rate sufficiently small at temperatures below about 400° to make the predominant reaction



But from consideration of the data obtained at various partial pressures and temperatures it was believed that this last reaction ought to be excluded. Accordingly, the results were regarded by v. Elbe as not sustaining the reaction scheme proposed for the mercury-sensitized hydrogen-oxygen reaction by Frankenburger and Klinkhardt which involved the recombination of 2OH to H_2O_2 .¹¹¹

The Photo-Oxidation of Hydrogen Iodide. Bates and Lavin¹¹² studied this reaction at pressures of 50-100 mm. of hydrogen iodide and 150-500 mm. of oxygen at 0°C. Their results led to the conclusion that the quasi-molecule HO_2 may have a life of 10^{-8} or 10^{-9} second, much longer than is usually assigned to such complexes. Kondrat'ev, Kondrat'eva and Lauris¹¹³ studied the effects of irradiating various mixtures of hydrogen iodide and oxygen both in Uviol apparatus transmitting only wave-lengths longer than 2800Å and in a quartz apparatus. A larger proportion of the hydrogen iodide was oxidized under the latter conditions. To explain the difference they assumed that in quartz along with the reaction $H + O_2 \longrightarrow HO_2$ there occurs the reaction $H + O_2 \longrightarrow OH + O$. Otherwise the results could be explained by assuming that the probability of occurrence of the reaction $HI + O_2 \longrightarrow HO_2$ increases with an increase in the kinetic energies of the hydrogen atoms and oxygen molecules.

Bodenstein and Schenk¹¹⁴ pointed out that the results of Bates and Lavin might be explained equally well on the assumption that the reaction between H and O_2 occurs as either two-body or three-body collisions. Kinetic studies by Cook and Bates¹¹⁵ indicated the reaction to be of the latter type, the third body being chiefly either oxygen or hydrogen iodide molecules. The presence of an inert gas such as nitrogen speeds up the reaction. In similar experiments, it was shown that deuterium iodide is always more completely oxidized than is hydrogen iodide.

Winther¹¹⁶ studied the rate of oxidation of hydriodic acid in the light and in the dark in various solvents.

PHOTOCHEMICAL REACTIONS OF THE OXIDES OF CHLORINE

Chlorine Monoxide. Balard, the discoverer of chlorine monoxide, observed its decomposition in light into chlorine and oxygen.¹¹⁷ Bodenstein and Kistiakowsky¹¹⁸ found that one absorbed quantum (4050 or 4360Å) caused the decomposition of two molecules of the monoxide, whether the quantum was absorbed by chlorine monoxide or by some chlorine also present. The reaction was unaf-

¹¹¹ Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc.*, **27**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932).

¹¹² Bates, J. R., and Lavin, G. I., *J. Am. Chem. Soc.*, **55**, 81, (1933).

¹¹³ Kondrat'ev, V., Kondrat'eva, E., and Lauris, A., *J. Phys. Chem. (U.S.S.R.)*, **5**, 1411 (1934); *Chem. Abs.*, **29**, 7810 (1935).

¹¹⁴ Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, **20B**, 420 (1933).

¹¹⁵ Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935); see also Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

¹¹⁶ Winther, C., *Z. physik. Chem.*, **113**, 275 (1924); **3B**, 209, 315 (1929); see also Plotnikow, I., *Ibid.*, **111**, 171 (1924).

¹¹⁷ Balard, A., *Ann. Pharm.*, **14**, 167, 298 (1835).

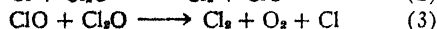
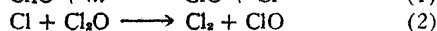
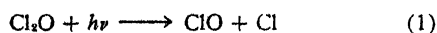
¹¹⁸ Bodenstein, M., and Kistiakowsky, G. B., *Z. physik. Chem.*, **116**, 371 (1925).

fectured by the presence of air and the temperature coefficient was 1.09. Small amounts of chlorine dioxide were formed during the decomposition. Schumacher and Wagner¹¹⁹ proposed a mechanism for the reaction in which ClO appears as an intermediate product.

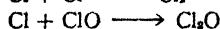
The absorption spectrum of chlorine monoxide is continuous from 2200 to 8500Å, so that dissociation is implied. The extinction coefficients have different values in various wave-length regions. Attempts have been made to assign different dissociation processes to different wave-length regions.¹²⁰

Goodeve and Wallace considered three types of dissociation, yielding respectively, Cl₂ and O, ClO and Cl, and Cl, Cl and O. Finkelnburg, Schumacher and Stieger, however, disregard the first possibility and believe that the absorption beginning at 6600Å corresponds to the second of these possibilities of dissociation, the chlorine atom probably being excited. Maxima apparent at 5300 and at 4100Å were attributed to the same dissociation products but in different states of excitation. Both groups of workers attribute the maximum at 2560Å to dissociation into an oxygen atom and two chlorine atoms.

For the wave-lengths 436, 365 and 313 mμ, the rate of decomposition is proportional to the amount of light absorbed, and therefore, independent of the chlorine pressure and also of the Cl₂O pressure until the latter falls below a certain limit. Finkelnburg, Schumacher and Stieger found a higher value than Bodenstein and Kistiakowsky for the quantum yield. It was about 3.5 and varied by only 10 per cent between the extreme wave-lengths. The temperature coefficient, (1.1 in agreement with Bodenstein and Kistiakowsky), increases as the temperature rises. The chain reaction observed was accounted for by the following processes:



Other intermediate products were noted to be ClO₂ and a brown higher oxide of chlorine of unknown composition. A smaller quantum yield observed when the reaction is conducted in solution in carbon tetrachloride¹²¹ was explained by Finkelnburg, Schumacher and Stieger on the assumption that the recombination reactions



occur so much more frequently in the solution than in the gaseous state that they compete effectively with reaction (2).

The use of shorter wave-lengths (2350-2750Å) increases the quantum yield to 4.5 at 20°C.¹²² The addition of hydrogen accelerates the decomposition, at least up to the stage at which the secondary reaction, H₂ + Cl₂ → 2HCl, becomes prominent.¹²³ Chlorine and oxygen are the main products. Hydrogen atoms are not as important as the ClO radical in continuing the chain, when the pressures of Cl₂O and H₂ are comparable.

The decomposition of chlorine monoxide can be effected by the 5460Å line

¹¹⁹ Schumacher, H. J., and Wagner, C., *Z. physik. Chem.*, **5B**, 199 (1929).

¹²⁰ Goodeve, C. F., and Wallace, J., *Trans. Faraday Soc.*, **26**, 254 (1930); Finkelnburg, W., Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **15B**, 127 (1931).

¹²¹ Dickinson, R. G., and Jeffreys, C. E. P., *J. Am. Chem. Soc.*, **52**, 4288 (1930).

¹²² Schumacher, H. J., and Townsend, R. V., *Z. physik. Chem.*, **20B**, 375 (1933).

¹²³ Iredale, T., and Edwards, T. G., *J. Am. Chem. Soc.*, **59**, 761 (1937).

in the presence of bromine as photosensitizer; under these conditions, the quantum yield is 4.3.¹²⁴

Chlorine Dioxide. Absorption bands of chlorine dioxide, beginning in the blue and violet regions¹²⁵ and extending to about 2700Å, exhibit rotational fine structure only on the low-frequency side of 3750Å.¹²⁶ At this point they begin to become diffuse because of predissociation. Schumacher believes a normal oxygen and ClO radical are produced and that at wave-lengths shorter than the convergence limit (2650Å by extrapolation), the O atom is liberated in the excited state (¹D). Bowen reported the photodecomposition of the dioxide¹²⁷ to produce chlorine, oxygen and Cl₂O₆. Spinks, who secured similar products,¹²⁸ found light in the blue and ultraviolet regions equally effective for photodecomposition. Since chlorine dioxide does not absorb at 5460Å, this wave-length is ineffective photochemically, except in the presence of bromine when a sensitized reaction occurs with a quantum efficiency practically equal to that produced by the 3650Å line.

In later studies,¹²⁹ it was shown that in the presence of moisture the reaction is more regular than in the case of the dry gas. The quantum efficiencies for the moist gas are 3.7 at 3650Å (predissociation region) and 3.1 at 4360Å (excited molecule region). No atomic chlorine is formed. For low concentrations of chlorine dioxide the yield is independent of concentration and light intensity. In dry gas at 17°, the pressure decreases as Cl₂O₆ is formed and condenses on the walls.¹³⁰ The reaction is sensitive to temperature changes. At 30°, the pressure increases owing to the decomposition of Cl₂O₆ which yields chlorine and oxygen. In aqueous solutions, at concentrations of chlorine dioxide below 8 per cent, the rate of decomposition is proportional to the light intensity. In the solution there can be detected hypochlorite, chlorate and perchlorate ions.

PHOTOCHEMICAL REACTIONS OF CARBON COMPOUNDS

Photolysis of Carbon Dioxide. A 15-mm. layer of carbon dioxide at atmospheric pressure exhibits a series of absorption bands beginning at about 1710Å (or somewhat longer wave-lengths); these apparently are superposed upon a continuum, possibly indicative of dissociation into carbon monoxide and oxygen.¹³¹ Chapman, Chadwick and Ramsbottom¹³² showed that after long intermittent illumination, dry carbon dioxide at atmospheric pressure was decomposed to the extent of 2.6 to 3 per cent. This decomposition was estimated by determining the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonized. When very carefully dried carbon dioxide was used, it was claimed that as much as 46 per cent could be decomposed in 45 hours. No decomposition whatever could be detected as a result of the irradiation of moist gas.

¹²⁴ Brown, A. G., and Spinks, J. W. T., *Canadian J. Research*, 15B, 113 (1937).

¹²⁵ Mayer, H., *Z. physik. Chem.*, 113, 220 (1924); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, 25, 738 (1929); Goodeve, C. F., and Wallace, J., *Ibid.*, 26, 259 (1930); Ku, Z. W., *Phys. Rev.*, 44, 376 (1933).

¹²⁶ Urey, H. C., and Johnston, H., *Phys. Rev.*, 38, 2131 (1931); Schumacher, H. J., and Finkelnburg, W., *Z. physik. Chem. Bodenstein Band*, 704 (1931).

¹²⁷ Bowen, E. J., *J. Chem. Soc.*, 123, 2328 (1923); Booth, H., and Bowen, E. J., *J. Chem. Soc.*, 127, 510 (1925).

¹²⁸ Spinks, J. W. T., *J. Am. Chem. Soc.*, 54, 1689 (1932); 55, 428 (1933).

¹²⁹ Spinks, J. W. T., and Porter, J. M., *J. Am. Chem. Soc.*, 56, 264 (1934).

¹³⁰ See also Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.*, 147, 233 (1925).

¹³¹ Leifson, S. W., *Astrophys. J.*, 63, 82 (1926).

¹³² Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, 91, 942 (1907); 89, 22 (1906).

The effect of water upon the reaction was verified by Coehn and Sieper.¹³³ The water underwent no change and neither formic acid nor formaldehyde was formed. It was also observed that the photolysis of dry carbon dioxide by radiations shorter than 2540Å occurs at a rate inversely proportional to the pressure. A final stationary state is eventually reached. These authors claimed also that some formaldehyde is produced during the irradiation of a mixture of equal volumes of carbon dioxide and hydrogen.

More recently, Coehn and Spitta¹³⁴ confirmed and extended the observations on the effect of water upon photolysis of carbon dioxide. They concluded that optimum decomposition at a pressure of 300 mm. occurs in the presence of a very small proportion of water; the addition of larger quantities of moisture or further drying was believed to reduce the decomposition. These conclusions were based upon the observation that 1 per cent decomposition occurred in a sample dried over sulfuric acid, but that a gas which had been in prolonged contact with phosphorus pentoxide was not altered on irradiation. Drying by liquid air reduced the decomposition to 1 per cent but in this gas the addition of a very small quantity of moisture and subsequent ultraviolet irradiation produced a decomposition of 10.5 per cent. Coehn and May¹³⁵ have more recently confirmed the inability of ultraviolet light to cause a decomposition in extremely dry carbon dioxide. The xenon lamp decomposes carbon dioxide with a quantum yield of 0.98.¹³⁶

It has been stated by Zenghalis¹³⁷ that the reduction of carbon dioxide in aqueous solution by very finely divided hydrogen takes place very slowly in the dark, but is markedly accelerated by sunlight and still more so by ultraviolet rays. In all cases the formaldehyde first produced undergoes polymerization.^{137a}

Carbon Monoxide. Although the band spectrum of this gas has been much studied, its complexities are of little photochemical significance.¹³⁸ A series of bands extends from about 2064.5Å to 920Å. The absorption is but slight at wavelengths longer than 1546Å. No continuous region is recorded since the heat of dissociation into normal atoms is too great for this process to occur in any readily available spectral region. There may be a predissociation limit at 1063Å. Hardeck, Groth and Faltings¹³⁹ find irradiation with the line 1295Å (but not with 1470Å) leads to the formation of carbon dioxide and carbon suboxide.

Thiele¹⁴⁰ observed that carbon monoxide and oxygen unite less readily under ultraviolet irradiation than do hydrogen and oxygen. Coehn and Tramm¹⁴¹ reported that the presence of moisture has no effect on union of carbon monoxide and oxygen. Exposure of moist and various dried mixtures to the radiations from a quartz mercury arc led to practically the same result, combination occurring to the extent of 4 or 5 per cent within an hour. There was, however, some effect of moisture upon the degree of explosibility of the gas mixtures when treated by a spark. A moist mixture could be exploded by a spark at any pressure. A

¹³³ Coehn, A., and Sieper, G., *Z. physik. Chem.*, **91**, 347 (1916).

¹³⁴ Coehn, A., and Spitta, T., *Z. physik. Chem.*, **9B**, 401 (1930).

¹³⁵ Coehn, A., and May, B. W., *Z. physik. Chem.*, **26B**, 117 (1934).

¹³⁶ Groth, W., *Z. physik. Chem.*, **37B**, 307, 315 (1937).

¹³⁷ Zenghalis, C. D., *Compt. rend.*, **171**, 167 (1920); *J. Soc. Chem. Ind.*, **39**, 596A (1920).

^{137a} For the sensitized reaction between carbon dioxide and water, see Chapter 43.

¹³⁸ Birge, R. T., and Hopfield, J. J., *Phys. Rev.*, **29**, 922 (1927); Leifson, S. W., *Astrophys. J.*, **63**, 82 (1926); Duffendack, O. S., and Fox, G. W., *Nature*, **118**, 12 (1926); Johnson, R. C., *Nature*, **118**, 50 (1926); Coster, D., and Brons, F., *Physica*, **1**, 155 (1934); Schmid, R., *Physik. Z.*, **37**, 55 (1936).

¹³⁹ Hardeck, P., Groth, W., and Faltings, K., *Z. Elektrochem.*, **44**, 621 (1938).

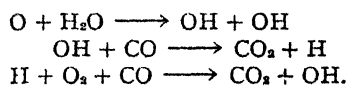
¹⁴⁰ Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).

¹⁴¹ Coehn, A., and Tramm, H., *Ber.*, **54**, 1148 (1921).

mixture dried by short exposure to solid carbon dioxide and alcohol could not be exploded, but burned quietly. A mixture which had been cooled for a sufficient time could not be ignited, although a pale bluish zone appeared around the spark gap and slight combination was indicated by a small diminution in pressure.

An increase in the temperature coefficient with temperature was observed by Kistiakowsky.¹⁴² This report and the fact that the gas mixture can be made to explode suggested to Jackson¹⁴³ that chain reactions are set up. The lack of absorption by carbon monoxide requires that the reaction produced by the 1720A line group of aluminum be explained by a primary dissociation of oxygen molecules. Since the yield of ozone was found to be about the same in mixtures of oxygen with either carbon monoxide or nitrogen, Jackson concluded that the efficiency of the process $O + CO \rightarrow CO_2$ must be at least 150 times lower than that of the reaction $O + O_2 \rightarrow O_3$. The activation energy of the first reaction is at least 3 kcal. greater than that of the latter, providing the steric factors influencing the efficiency of the collisions are the same in both cases. Hardeck and Kopsch¹⁴⁴ have reported a similar unreactivity of oxygen atoms (from a discharge tube) toward carbon monoxide.

At high temperatures (500-550°C.), the dry oxidation of carbon monoxide is practically independent of temperature and total pressure. When water is present, the rate depends on the total pressure and has a large temperature coefficient. In the presence of water, the following chain may be set up, according to Jackson,



The last two reactions had been suggested by Farkas, Haber and Hardeck¹⁴⁵ to explain the photosensitizing action of ammonia in the oxidation of carbon monoxide. The primary photodissociation of the ammonia produces NH_2 and a hydrogen atom, the latter starting the last reaction. It has subsequently been found by Jackson¹⁴⁶ that at high temperatures, hydrogen peroxide is also formed in the presence of moisture.¹⁴⁷

Popov¹⁴⁸ studied the oxidation of carbon monoxide at pressures as low as 0.01-1.5 mm. of mercury and at temperatures up to 150°. He found the reaction of carbon monoxide and atomic oxygen to be heterogeneous and to have a very small energy of activation. Contrary to the case of the oxidation of carbon monoxide by atomic oxygen obtained by means of a discharge, the efficiency of wall collisions was found to be large. This efficiency could be explained by assuming the participation of metastable 1D oxygen atoms, which are obtained along with normal state atoms during the photodissociation of molecular oxygen. The reaction is then $CO_{ads.} + O' \rightarrow CO_2$ for the principal process. A correlation between the constants for the kinetic expression for this reaction and the isotherm of the adsorption of carbon monoxide on quartz could be shown.

¹⁴² Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

¹⁴³ Jackson, W. F., *J. Am. Chem. Soc.*, **56**, 2631 (1934).

¹⁴⁴ Hardeck, P., and Kopsch, U., *Z. physik. Chem.*, **12B**, 327 (1931).

¹⁴⁵ Farkas, L., Haber, F., and Hardeck, P., *Naturwiss.*, **18**, 266 (1930); *Z. Elektrochem.*, **36**, 711 (1930).

¹⁴⁶ Jackson, W. F., *J. Am. Chem. Soc.*, **57**, 82 (1935).

¹⁴⁷ It has recently been claimed that the interposition of an oxygen filter does not affect the rate of the reaction, although a carbon monoxide filter decreases it. Ziskin, M., Kondrat'ev, V., and Sushkevitch, T., *J. Phys. Chem. (U.S.S.R.)*, **8**, 281 (1936); *Chem. Abs.*, **31**, 1297 (1937).

¹⁴⁸ Popov, B., *Acta Physicochim. U.R.S.S.*, **3**, 223 (1935); *Chem. Abs.*, **30**, 2109 (1936).

The mercury-sensitized reaction between hydrogen and oxygen, in the presence of carbon monoxide, was studied by Barak and Taylor.¹⁴⁹ With equal concentrations of hydrogen and carbon monoxide, the former is oxidized five times as rapidly as the latter. When the hydrogen to carbon monoxide ratio was five to one, 20 per cent of the carbon monoxide formed formaldehyde. Reaction between hydrogen and carbon monoxide occurred at 18 per cent of the rate of that between hydrogen and oxygen in electrolytic gas. These results are consistent with an initial exclusive formation of hydrogen peroxide and a chain reaction with a mean chain-length of approximately six. In similar work, Farkas and Sachsse¹⁵⁰ found hydrogen atoms to combine with carbon monoxide molecules in three-body collisions to yield HCO. If the back reaction takes place and 0.1 of the three-body collisions are effective in the formation of the radical, the ratio of formation to decomposition at room temperatures is 1/370.

The phosgene-sensitized oxidation of carbon monoxide by the unfiltered radiations of the mercury arc has been investigated by Rollefson and Montgomery.¹⁵¹ They gave the rate expression for low oxygen pressures as

$$\frac{d(\text{CO}_2)}{dt} = k\sqrt{I_0[\text{COCl}_2][\text{CO}][\text{O}_2]}$$

At higher oxygen pressures, the rate becomes independent of the oxygen pressure. These authors suggested that the mechanism of this reaction is very similar to that of the chlorine-sensitized reaction.¹⁵²

The latter is quite complicated, a thousand molecules of carbon dioxide per quantum being formed in mixtures of a half atmosphere each of chlorine, carbon monoxide and oxygen. In blue light at high pressures and in large vessels, the rate of production of carbon dioxide is proportional to the chlorine concentrations and to the square root of that of carbon monoxide. For small pressures and vessels with a large surface, it is proportional to the square root of the concentrations of carbon monoxide and chlorine.

In the presence of nitric oxide, a small proportion of the carbon monoxide present is, on irradiation by ultraviolet rays, converted into carbon dioxide by interaction with oxygen liberated from the nitric oxide.¹⁵³

In the decomposition of carbon monoxide in the silent electric discharge a brown solid not identical with polymerized carbon suboxide is formed.¹⁵⁴

THE PHOTOCHEMISTRY OF PHOSGENE

Formation of Phosgene. The formation of phosgene from carbon monoxide and chlorine, reported by Davy in 1812,¹⁵⁵ is somewhat analogous to the combination of hydrogen and chlorine in that the reaction has a very high quan-

¹⁴⁹ Barak, M., and Taylor, H. S., *Trans. Faraday Soc.*, **28**, 569 (1932); for early observations see Hercheffinkel, H., *Compt. rend.*, **149**, 395 (1909). See also page 257.

¹⁵⁰ Farkas, L., and Sachsse, H., *Z. physik. Chem.*, **27B**, 111 (1934).

¹⁵¹ Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55**, 4036 (1933)

¹⁵² For a full discussion of the reaction schemes proposed for the latter, see Schumacher, H. J., and Stieger, G., [*Z. physik. Chem.*, **13B**, 157 (1931)]; Warming, E., [*Z. physik. Chem.*, **18B**, 153 (1932)]; Schumacher, H. J., [*Z. physik. Chem.*, **18B**, 155 (1932)]; and Franke, W. K., and Schumacher, H. J., [*Ibid.*, **B40**, 115 (1938)].

¹⁵³ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 129 (1913).

¹⁵⁴ Crespi, M., and Lunt, R. W., *J. Chem. Soc.*, **127**, 2052 (1925); Lunt, R. W., and Mumford, L. S., *J. Chem. Soc.*, 1711 (1929).

¹⁵⁵ Davy, H., *Phil. Trans.*, **30**, 144 (1812).

tum yield, is under certain conditions inhibited by oxygen and is to a high degree subject to the influence of traces of impurities which give rise to induction periods.¹⁵⁶

Details of the kinetics of this reaction were reported by Bodenstein.¹⁵⁷ The results with various mixtures of carbon monoxide and chlorine were complicated and for a considerable time considered to be affected by traces of moisture present. It was established that oxygen retards the reaction until near completion of the latter, when its effect suddenly decreases. The oxygen is consumed by a chlorine-sensitized reaction in which carbon monoxide is oxidized to the dioxide. Carbon dioxide formation is proportional to the carbon monoxide pressure, increases with the chlorine pressure, but more slowly than in direct proportion, and decreases with increasing oxygen concentration, but not so rapidly as to be inversely proportional to the latter. At room temperature, the rate of formation of phosgene was found to be proportional to the chlorine concentration, to the square root of the absorbed energy and to the square root of the carbon monoxide concentration. The temperature coefficient near room temperature is unity or slightly less.

Subsequent work by Bodenstein and Onoda¹⁵⁸ revealed that the order of reaction is different at temperatures between 200° and 300°C. The rate of formation of the phosgene is then directly proportional to the absorbed energy, and to the concentrations of the reactants (chlorine and carbon monoxide). At these temperatures, furthermore, the retarding effect of oxygen is no longer observable. At 300°C. no formation of carbon dioxide occurs in the presence of oxygen. Between 270° and 300°C., the velocity coefficient is considerably influenced by hydrolysis of phosgene by water vapor, but at the higher temperatures all the water vapor appears to be removed in the early stages of the reaction. A poisoning effect of small quantities of carbon dioxide in the reaction at ordinary temperatures was demonstrated by Cathala.¹⁵⁹ The effect is diminished when wavelengths shorter than 3500A are employed in the irradiation.

As in the case of the hydrogen-bromine reaction, a mechanism to account for the kinetics of the reaction was developed by Bodenstein¹⁶⁰ by extending the mechanism used to account for the thermal reaction. The result was a succession of processes which involved excited chlorine and carbon monoxide molecules, as well as the chlorine atoms and triatomic chlorine molecules which are assumed to play a part in the thermal process. Although the introduction of a few assumptions regarding the rate constants of the partial reactions permitted a fairly satisfactory derivation of an expression similar to the experimental rate expression, the Bodenstein formulation has since been superseded by others which avoid the assumption of excited chlorine molecules as the products of the primary process.

A primary photodissociation of chlorine molecules was made the first step in the formulation of Bodenstein, Lenher and Wagner¹⁶¹ which was based on an investigation of the reaction at low total pressures (below 40 mm.) and at ordinary temperatures. The partial reactions proposed were the following:

¹⁵⁶ Chapman, D. L., and Gee, F. H., *J. Chem. Soc.*, **99**, 1726 (1911); Dyson, G., and Harden, A., *J. Chem. Soc.*, **83**, 201 (1903). For a general review, see Kistiakowsky, G. B., *Z. angew. Chem.*, **44**, 602 (1931). Early kinetic measurements were reported by Wildermann, M., *Phil. Trans.*, **199A**, 337 (1902); *Z. physik. Chem.*, **42**, 257 (1903).

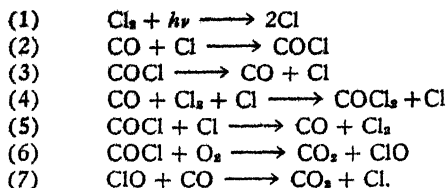
¹⁵⁷ Bodenstein, M., *Rec. trav. Chim.*, **41**, 585 (1922).

¹⁵⁸ Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131**, 153 (1928).

¹⁵⁹ Cathala, J., *J. chim. phys.*, **24**, 663 (1927).

¹⁶⁰ Bodenstein, M., *Sitzb. Preuss. Akad.*, **13**, 104 (1926); *Z. physik. Chem.*, **130**, 422 (1927); Schumacher, H. J., *Z. physik. Chem.*, **129**, 241 (1927).

¹⁶¹ Bodenstein, M., Lenher, S., and Wagner, C., *Z. physik. Chem.*, **3B**, 459 (1929).



The last two reactions were employed only to account for the inhibiting action of oxygen and the sensitized formation of carbon dioxide. In this scheme there is supposed to be an equilibrium between the hypothetical COCl molecule and its decomposition products. The phosgene is formed only by the triple collisions in (4); it is to be noted that (4) is a chain reaction and accounts for the high quantum yield. By making the formation of phosgene depend upon a reaction involving triple collisions, the slowness of reaction at low pressures could be accounted for. In addition to processes (2) and (5), which represent removal of chlorine atoms in the gas phase, both COCl and Cl diffuse to the walls of the vessel where recombination occurs. Processes involving water were not included since Schultze¹⁶² found the previously much-discussed effect of traces of moisture to be non-existent. By a treatment of these partial reactions in a manner analogous to that discussed in the section on hydrogen bromide, it can be shown that the rate constant is (as experimentally found) a function of the square root of the intensity of the light.

Lenher and Rollefson,¹⁶³ however, objected to the assumption of an equilibrium between COCl and CO and Cl on the ground that the hypothetical intermediate should be expected to react with chlorine as well as with oxygen. They assumed the phosgene to be formed by the process $\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$. Furthermore, the formation of the intermediate was believed to occur through a triple collision: $\text{CO} + \text{Cl} + \text{M} \rightarrow \text{COCl}$, in which chlorine molecules may function as the inert molecule with a relatively high efficiency. The rate of formation of phosgene was believed to be so fast compared to the rate of decomposition of COCl that the former may be considered the determining factor in fixing the concentration of the intermediate.

To account for the change in reaction order at 300°C. observed by Schumacher,¹⁶⁴ Lenher and Rollefson consider that the decomposition of COCl into Cl and CO is very rapid at this temperature. The equilibrium concentration of this intermediate (COCl) is very small, under which condition the chain-breaking reactions (6) and (7) have very small rates. The low steady state of COCl makes it necessary to assume for the formation of the phosgene reaction (4) of the Bodenstein, Lenher and Wagner mechanism. At room temperatures, reaction (4) is supposed to be subordinate to the process: $\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$. At high temperatures, chlorine atoms can only be removed by recombination at the wall or by collisions in the gas phase, rather than by combination with COCl. Therefore, the concentration of chlorine atoms becomes sufficient to permit of the formation of phosgene by the Bodenstein reaction. Schumacher and Stieger¹⁶⁵ showed that at temperatures above 250°C. and also at room temperatures when the total pressures were below one atmosphere or the vessels used had relatively large

¹⁶² Schultze, G., *Z. physik. Chem.*, **5B**, 368 (1929).

¹⁶³ Lenher, S., and Rollefson, G. K., *J. Am. Chem. Soc.*, **52**, 500 (1930).

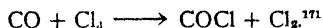
¹⁶⁴ Schumacher, H. J., *Z. physik. Chem.*, **129**, 241 (1927).

¹⁶⁵ Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **13B**, 157 (1931).

surfaces, a considerable portion of the chlorine atoms recombine on the walls of the vessel. The new mechanism is adequate to describe the rate of formation of phosgene under these conditions.

Schumacher,¹⁶⁶ as well as Warming,¹⁶⁷ however, defended the mechanism of Bodenstein, Lenher and Wagner. They believe the rate of formation of COCl by triple collisions to be reasonably fast at ordinary pressures and state that the heat of formation of this molecule is so low that the decomposition must proceed at a rapid rate. Rollefson¹⁶⁸ asserts that it is impossible for COCl to attain its equilibrium concentration since other reactions, for example, between Cl₂ and COCl, occur too rapidly. The distinction is that in the Rollefson mechanism the COCl molecule may react either with chlorine or oxygen, the relative amounts of the two being determined by the specific rate constants and the relative pressures of the gases. On the other hand, in the Bodenstein mechanism it was postulated that only the oxygen could react with the COCl. The latter molecule was assumed to be in equilibrium with its dissociation products in the absence of oxygen, but not in its presence. The relative amounts of carbon dioxide and phosgene formed will depend upon the manner in which the COCl molecules divide between the two paths open to them. Increase of the pressure of oxygen at a definite pressure of chlorine should cause a decrease in the amount of phosgene formed and preliminary experiments appeared to indicate this to be the case. Rollefson¹⁶⁹ stated later that the specific rates for the two reactions destroying COCl are of the same order of magnitude. The phosgene formation has a higher temperature coefficient and therefore higher energy of activation than that leading to the formation of carbon dioxide. The relative amounts of the two reactions is a function solely of the ratio of chlorine to oxygen at constant temperature.

In a more recent paper, however, Rollefson¹⁷⁰ concludes that the active form of chlorine involved in the chain process is probably triatomic chlorine and believes the intermediate to be formed by



Recently, the reaction has been restudied by Bodenstein, Brenschede and Schumacher,¹⁷² using very pure gases over a wide concentration range. The mercury line 4358A was used for the reaction at 14-16°C., pressure measurements being made with a quartz spiral manometer. Evidence was given to show that COCl rather than Cl₃ is the intermediate at chlorine pressures between 340 and 180 mm. Below this and down to 15 mm., there was evidence for an additional chain-breaking mechanism $\text{H} + \text{COCl}_2 \rightarrow \text{HCl} + \text{COCl}$ on the wall, and another method of phosgene formation. Also,¹⁷³ they have investigated the induction and after-periods by a rotating sector method, and found the resulting rate changes in agreement with those calculated from their mechanism. If the gases were not free from oxygen, the after-effects were five times as large. Oxygen inhibits the

¹⁶⁶ Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 3132 (1930).

¹⁶⁷ Warming, E., *Z. physik. Chem.*, **18B**, 156 (1932).

¹⁶⁸ Rollefson, G. K., *Trans. Faraday Soc.*, **27**, 465 (1931).

¹⁶⁹ Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 148 (1933).

¹⁷⁰ Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 579 (1934); see also Rollefson, G. K., and Eyring, H., *J. Am. Chem. Soc.*, **54**, 170 (1932); Rollefson, G. K., *Z. physik. Chem.*, **37B**, 472 (1937).

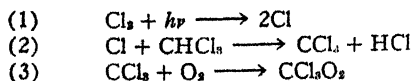
¹⁷¹ Cathala, J., *J. chim. phys.*, **25**, 182 (1928) had previously assumed the phosgene to be formed by the reaction: $\text{Cl}_3 + \text{CO} \rightarrow \text{COCl}_2 + \text{Cl}$

¹⁷² Bodenstein, M., Brenschede, W., and Schumacher, H., *Z. physik. Chem.*, **28B**, 81 (1935); **40B**, 121 (1938).

¹⁷³ Bodenstein, M., Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **35B**, 382 (1937); See also Taylor, H. S., *J. Phys. Chem.*, **42**, 789 (1938).

stationary formation of phosgene, but does not affect the equilibrium: $\text{COCl} \rightleftharpoons \text{CO} + \text{Cl}$. This indicates the possible presence of an oxygen-containing intermediate compound with a longer life than either Cl or COCl.

The photochemical formation of phosgene from chloroform and oxygen (sensitized by chlorine) has been found to occur by Schumacher and Wolff.¹⁷⁴ The following mechanism is proposed:



The last compound forms phosgene and also breaks the chains. The quantum yield at 65° and a chloroform pressure of 100 mm. is 260 moles per einstein. The chain-breaking process can be neither a three-body collision nor diffusion to the walls since the rate is independent of the pressure. It is proportional to the absorbed light and to the square root of the chloroform concentration. The temperature coefficient is 1.23. The reaction is not influenced by hydrogen chloride or phosgene. It is almost completely inhibited by alcohols or ammonia, these substances being chlorinated and then decomposing. Completely chlorinated substances do not inhibit the reaction.¹⁷⁵

Decomposition of Phosgene. Absorption data by Henri and Howell¹⁷⁶ indicated a region of absorption bands of phosgene to begin at 3041Å. The bands become diffuse at 2750Å and extend to 2380Å beyond which the absorption becomes continuous. When phosgene is heated to 100-200°C., an additional continuous spectrum overlays the bands.

Weigert¹⁷⁷ found irradiation of phosgene at 500°C. caused no displacement from the thermal equilibrium ratio of the gas and its decomposition products, and in this Bodenstein and Onoda¹⁷⁸ concur. At the ordinary temperatures, phosgene, passed through a quartz tube at the rate of 1 cc. per minute, was decomposed to the extent of 3.3 to 4 per cent.¹⁷⁹ In a Uviol tube permeable only to radiations of wave-length longer than 2650Å, the decomposition reached only 0.46-0.5 per cent. In ordinary glass tubes there was no decomposition. In each case the equilibrium could be approached from either side.

Almasy and Wagner-Jauregg¹⁸⁰ studied the decomposition of phosgene at 300 mm. pressure at both 20° and 160°C. in a quartz vessel surrounded by a mercury arc lamp. For isolating the region of bands a filter of 5 per cent benzene in hexane was used. To eliminate the effect of absorption by the liberated chlorine, the quartz vessel was surrounded by a chlorine filter. The contents of the vessel after irradiation were analyzed by freezing out the chlorine and phosgene and following the pressure change, or by titrating the chlorine and phosgene. The absorption of radiations in the region of sharp bands produced a decomposition to the extent of 0.25 to 1.75 per cent depending on the intensity of the light and the pressure of the phosgene. The decomposition was not increased at 160°C. It was assumed to be due to some process of predissociation and required no more

¹⁷⁴ Schumacher, H. J., and Wolff, K., *Z. physik. Chem.*, **16B**, 453 (1934).

¹⁷⁵ Schumacher, H. J., and Sundhoff, D., *Z. physik. Chem.*, **34B**, 300 (1936).

¹⁷⁶ Henri, V., and Howell, O. R., *Proc. Roy. Soc.*, **128**, 192 (1930).

¹⁷⁷ Weigert, F., *Ann. Physik*, **24**, 55 (1907).

¹⁷⁸ Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131**, 153 (1928).

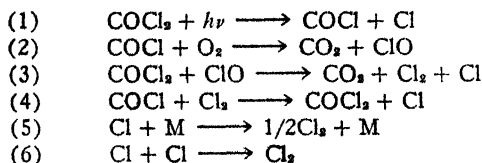
¹⁷⁹ Coehn, A., and Becker, H., *Ber.*, **43**, 130 (1910).

¹⁸⁰ Almasy, F., and Wagner-Jauregg, T., *Naturwiss.*, **19**, 270 (1931); *Z. physik. Chem.*, **19B**, 405 (1932).

han 100 kcal. The use of the entire mercury arc spectrum increased the decomposition to 2.19 to 8.65 per cent. Under these conditions the decomposition was nearly doubled at 160°C. Rollefson and Montgomery,¹⁸¹ found that in the presence of oxygen, the rate of formation of carbon dioxide was directly proportional to the phosgene concentration and to the incident light intensity at either 20°, 90° or 200°C. At higher oxygen pressures, the rate was independent of the oxygen concentration, but at lower pressures it gradually fell off with decreasing oxygen, the rate being a function of the chlorine-oxygen ratio rather than of the oxygen concentration itself. They derived the rate law

$$\frac{d(\text{CO}_2)}{dt} = \frac{kI_0(\text{COCl}_2)}{1 + k' \left(\frac{Cl_2}{O_2} \right)}$$

from the following series of reactions.



From the derivation it is apparent that the value of k' in the rate equation expressed the relative reactivity of the COCl molecule with chlorine and with oxygen. The average quantum yield of the decomposition was found to be 1.8. For the phosgene-sensitized oxidation of carbon monoxide they found quantum yields of 90 to 110, lower than those of others cited in the discussion of that reaction.¹⁸²

The exposure of mixtures of phosgene and hydrogen to ultraviolet radiation results in a much greater decomposition, up to 97 per cent, since liberated chlorine may combine with the hydrogen to form hydrogen chloride. Bredig and von Goldberger¹⁸³ failed in attempts to obtain formaldehyde according to the reaction: $\text{COCl}_2 + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + 2\text{HCl}$. At 10°C., minute traces were obtained, but there was none at all at 80°C. The walls of the reaction vessel were observed to be coated with a white to brown deposit.

Montgomery and Rollefson¹⁸⁴ found the initial rate of the decomposition in the presence of hydrogen to be rather insensitive to a tenfold variation in the pressure of the latter gas, although the initial rate showed a slight increase as the hydrogen pressure was increased. With increase in the phosgene pressure, the rate had an upward trend but appeared to approach a limiting value at high phosgene pressures. By plotting the initial rates against the calculated percentage of absorption of the 2537Å line (the most intense line beyond the predissociation limit) a straight line was obtained, indicating the rate to be a function of the first power of the absorbed light, as well as of the incident intensity. There was, however, a deviation from a simple first order law, since the rate of change of the logarithm of the phosgene concentration did not remain constant with time. In seeking the cause of this deviation, it was found that the rate is inversely proportional to, or at least involves a term which is inversely proportional to, the total

¹⁸¹ Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55**, 142 (1933).

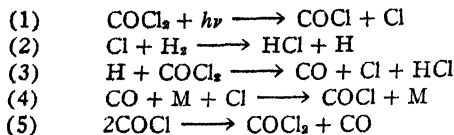
¹⁸² Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4025 (1933).

¹⁸³ Bredig, G., and v. Goldberger, A., *Z. physik. Chem.*, **110**, 521 (1924).

¹⁸⁴ Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4030 (1933).

pressure as varied by the addition of carbon dioxide or nitrogen. This effect was more pronounced when carbon monoxide was the added gas, in which case there was some evidence that the carbon monoxide concentration enters the rate law explicitly. It appeared likely that the deviation from first order may depend upon the ratio of added hydrogen to added carbon monoxide when both are added.

From the reaction mechanism

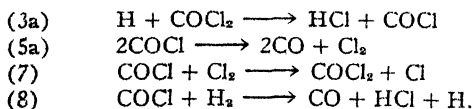


it was possible to derive the rate equation

$$\frac{d(\text{CO})}{dt} = I_0(\text{COCl}_2) \left[1 + \frac{k_2(I_{\text{H}_2})}{k_4(\text{CO})(\text{M})} \right]$$

which seemed in agreement with the experimental facts. The second term makes its largest contribution to the rate at the start of the reaction, and the first two or three values of the divergence from a first order reaction are always larger than succeeding values. It also appeared that the quantum yield was 3.7 at two minutes, decreasing to 2.4 at eight minutes. The concentration of M (any molecule capable of taking up the excess energy of COCl and so stabilizing it) was assumed equal to the total pressure. This would be the case if all kinds of molecules present are equally capable of acting in this way, even though carbon monoxide may have a more pronounced effect than nitrogen. The absence of formaldehyde formation was attributed to the non-reactivity of COCl toward hydrogen. This non-reactivity is believed to cause an increase in the concentration of COCl so that reaction (5) becomes the chain-terminating process.

Kassel¹⁸⁵ found an error in the derivation of the rate law in that the rate of production of CO in (5) was erroneously taken as equal to the rate of consumption of COCl in this step. If this is corrected, the 1 within the bracket of the final rate equation drops out and agreement with experiment is lost. Kassel suggested the mechanism:



This leads to the rate equation

$$\frac{d(\text{CO})}{dt} = \frac{2I_{\text{abs}}k_2(\text{H}_2)}{k_2(\text{H}_2) + k_4(\text{CO})(\text{M})} + k_5\sqrt{I_{\text{abs}}/k_{8a}}(\text{H}_2)$$

Some work has been done on the photochemistry of bromophosgene. Trautz¹⁸⁶ had stated that the bromo compound could be formed photochemically. However, Schumacher and Bergmann,¹⁸⁷ who irradiated mixtures of carbon monoxide and bromine with different portions of the spectrum, concluded that at tempera-

¹⁸⁵ Kassel, L. S., *J. Am. Chem. Soc.*, **56**, 243 (1934).

¹⁸⁶ Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).

¹⁸⁷ Schumacher, H. J., and Bergmann, P., *Z. physik. Chem.*, **13B**, 269 (1931).

ures less than 100°C., neither excited bromine molecules nor bromine atoms react with carbon monoxide to form bromophosgene. Furthermore, when mixtures of bromophosgene and bromine were irradiated with light in the absorption band region of bromine, no pressure change was noted. When irradiated in its own absorption region (3200-2100Å) bromophosgene is, however, decomposed with a quantum yield of unity. The reaction is of zero order and non-absorbing foreign gases do not affect the rate. The temperature coefficient is one for 10° between 0° and 40°C.

No reaction between carbon monoxide and fluorine could be detected when a mixture of these gases was irradiated in a quartz tube by ultraviolet rays.¹⁸⁸

THE PHOTOCHEMISTRY OF NITROGEN COMPOUNDS

The absorption by nitrogen has been studied by Birge and Hopfield¹⁸⁹ and y Sponer.¹⁹⁰ The spectrum consists of a system of bands beginning at 1450Å and extending to 1227Å. Excited molecules are formed. No photochemical reactions which can be attributed to this absorption are known as yet.

Ammonia. The ultraviolet absorption of this gas is limited to the region of wave-lengths shorter than about 2200Å or 2400Å. Between this limit and 1860Å is a region of absorption with a maximum at 1910-1935Å.¹⁹¹ This region comprises a series of diffuse predissociation bands, the investigation of which by Bonhoeffer and Farkas¹⁹² gave the first indication that predissociation in general implies a spontaneous decomposition. These workers were unable to observe fluorescence of light absorbed in this region, showing that the molecules excited by absorption did not persist long enough to emit energy spontaneously. By the use of the para-hydrogen method, Geib and Harteck¹⁹³ subsequently proved the presence of atomic hydrogen in ammonia which has absorbed radiations within this region.¹⁹⁴ The primary process appears to be a dissociation into NH₂ and H; recombination is rapid, and the concentration of hydrogen atoms is very small. Further spectroscopic evidence for this interpretation was found in the measurements and analysis by Dixon¹⁹⁵ of 16 strong bands between 1900 and 2400Å. Duncan¹⁹⁶ has shown that the diffuse predissociation bands continue to 1665Å, after which they become sharp and show rotational fine structure. True continuous absorption does not appear until about 1200Å. At 1150Å and below, the continuous absorption becomes so strong that the superposed sharp bands can no longer be measured accurately; the latter continue, however, at least down to 985Å. Electron impact studies of ammonia at electron accelerations corresponding to wave-lengths within this very short wave-length region have been reported by Waldie,¹⁹⁷ Bartlett,¹⁹⁸ and McLennan and Greenwood¹⁹⁹ but are of little

¹⁸⁸ Humiston, B., *J. Phys. Chem.*, **23**, 572 (1919); *Chem. Abs.*, **14**, 534 (1920).

¹⁸⁹ Birge, R. T., and Hopfield J. J., *Astrophys. J.*, **68**, 257 (1928); Hopfield, J. J., *Phys. Rev.*, **36**, 9 (1930).

¹⁹⁰ Sponer, H., *Proc. Nat. Acad. Sci.*, **13**, 100 (1927); *Z. Physik*, **41**, 611 (1927).

¹⁹¹ Landsberg, G., and Predvoditelev, A., *Z. Physik*, **31**, 544 (1925).

¹⁹² Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1928).

¹⁹³ Geib, K. H., and Harteck, P., *Z. physik. Chem. Bodenstein Band*, 861 (1931).

¹⁹⁴ Ammonia is also known to sensitize reactions in which atomic hydrogen is required. Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **12**, 267 (1930); Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **53**, 562 (1931).

¹⁹⁵ Dixon, J. K., *Phys. Rev.*, **43**, 711 (1933).

¹⁹⁶ Duncan, A. B. F., *Phys. Rev.*, **47**, 822 (1935).

¹⁹⁷ Waldie, A. T., *J. Frank. Inst.*, **200**, 507 (1925).

¹⁹⁸ Bartlett, J. H., Jr., *Phys. Rev.*, **33**, 169 (1928).

¹⁹⁹ McLennan, J. C., and Greenwood, G., *Proc. Roy. Soc.*, **120A**, 283 (1928).

significance for the photochemistry of ammonia. Experiments on the decomposition of ammonia in discharge tubes²⁰⁰ have also been indicative of the formation of atomic hydrogen and of some compound of hydrogen and nitrogen, NH_2 or NH .

Chemical evidence for the decomposition of ammonia by ultraviolet light was first advanced by Regener²⁰¹ and by Berthelot and Gaudechon.²⁰² Coehn and Prigent²⁰³ were unable to demonstrate a stationary state. Instead the decomposition appeared to go to completion within six hours. The ammonia was sealed in quartz tubes and irradiated with a quartz mercury arc. No ammonia could be demonstrated in a mixture of nitrogen and hydrogen, with or without chlorine as sensitizer, after irradiation with a quartz mercury arc. Noyes²⁰⁴ has found ammonia to be formed in small amounts when a mixture of nitrogen, hydrogen and mercury vapor is exposed at the boiling point of mercury to light from a quartz mercury arc. Only traces of hydrazine could be detected. The reaction has been attributed to the dissociation of hydrogen by the excited mercury atom.²⁰⁵

The quantum yield of the decomposition of ammonia at room temperature by wave-lengths 2025 to 2041 Å was found by Warburg²⁰⁶ to be 0.23-0.25. The rate of the decomposition was not affected by the addition of the decomposition products, even when so much of these were added as to make the ammonia but 5 per cent of the gas mixture. Kuhn²⁰⁷ found the rate proportional to the incident light intensity, and verified the observation that the quantum yield was independent of the ammonia pressure. The value of the yield was, however, 0.45, nearly twice that of Warburg. The yield could, however, be decreased to 0.10 by using light of only two spectral lines, 2063 and 2100 Å. At high temperatures (500°C.) the speed of decomposition was nine times as great as at 20°C. The quantum yield increased by about 50 per cent for every 100° increase in temperature, reaching 3.3 at 500°. At this temperature the rate of decomposition could be retarded by the addition of hydrogen, although nitrogen had no effect.

In a repetition of these experiments, Wiig and Kistiakowsky²⁰⁸ verified the Warburg values for the quantum yield at room temperature, 0.23, zinc spark, mean wave-length, 2090 Å, 0.24, aluminum spark, mean wave-length, 1962 Å, 0.25, cadmium spark, mean wave-length, 2144 Å. At 500°C. the quantum yield increased only to 0.48. They were inclined to attribute Kuhn's high value at 500°C. and his observation of a decrease in quantum yield when the monochromatic nature of the light was increased, to experimental error. They found further that the quantum yield is independent of the ammonia pressure over the range 1 to 800 mm. Also the quantum yield was not affected by seven fold variations in the intensity of the radiation or of seventeen-fold variations in the extent to which decomposition had occurred when the data were taken for the computations.

The use of radiations transmitted by fluorite but not by quartz increases the

²⁰⁰ Hutchinson, W. K., and Hinshelwood, C. N., *Proc. Roy. Soc.*, 117A, 131 (1927); Lavin, G. I., and Bates, J. R., *Nature*, 125, 709 (1930).

²⁰¹ Regener, E., *Preuss. Akad.*, 1228 (1904).

²⁰² Berthelot, D., and Gaudechon, H., *Compt. rend.*, 150, 1169, 1327, 1517, 1690 (1910); 155, 207 (1912); 156, 124 (1913).

²⁰³ Coehn, A., and Prigent, G., *Z. Elektrochem.*, 20, 275 (1914).

²⁰⁴ Noyes, W. A., Jr., *J. Am. Chem. Soc.*, 47, 1003 (1925).

²⁰⁵ For the synthesis of ammonia in an arc, see Storch, H. H., and Olson, A. R., *J. Am. Chem. Soc.*, 45, 1605 (1923); Olson, A. R., *Ibid.*, 48, 1298 (1926); Mochan, I., Roginskii, S., Fedorov, F., and Shekhter, A., *Compt. rend. acad. sci. (U.R.S.S.)*, 2, 365 (1934); *Chem. Abs.*, 28, 5339 (1934).

²⁰⁶ Warburg, E., *Sitzb. Preuss. Akad.*, 746 (1911); 216 (1912); 872 (1914).

²⁰⁷ Kuhn, W., *Compt. rend.*, 178 (1924); 177, 956 (1923); *J. chim. phys.*, 23, 521 (1926).

²⁰⁸ Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, 54, 1806 (1932).

quantum yield to 0.69, so that the yield appears to be higher in the region 1900-1600Å.²⁰⁹ The xenon lamp, however, gives a quantum yield of but 0.17.²¹⁰

Prior to the work of Bonhoeffer and Farkas on the nature of the predissociation process, evidence was advanced by both Dickinson and Mitchell²¹¹ and Taylor and Bates²¹² that was difficult to reconcile with the simple excited molecule mechanisms. These workers showed that the decomposition mixture contained more hydrogen (87-96 per cent) than would correspond to the stoichiometrical relation. This could be interpreted only as indicative of the formation of some hydrazine. Bates and Taylor suggested that excited ammonia molecules might either react with normal molecules to produce hydrazine and ammonia or that they might spontaneously yield atomic hydrogen and NH_2 radicals, the latter then forming hydrazine and atomic hydrogen by reaction with ammonia, or reforming ammonia and atomic hydrogen by reacting with hydrogen molecules.

At present, the NH_2 molecules, which are responsible for the formation of hydrazine, are regarded as arising from the predissociation of ammonia. Not much hydrazine is formed when ammonia is irradiated at room temperatures. Wiig and Kistiakowsky even found the composition of the resulting gases to be the same as that formed in the thermal decomposition, that is, close to a 1:3 nitrogen: hydrogen ratio. Koenig and Brings²¹³ studied the formation of hydrazine at temperatures of -80°C . in the glow discharge, but found that the yield, referred to the electrical energy consumed, was smaller than that with flowing gas at room temperature. Irradiation by the zinc spark caused not only formation but also decomposition of hydrazine, so that only traces could be obtained. They believed hydrazine to be formed in larger amount by the reaction $\text{NH}_3 + \text{NH} \rightarrow \text{N}_2\text{H}_4$ than by direct combination of two NH_2 radicals. Gedye and Rideal²¹⁴ claimed the yield could be increased by employing low temperatures, a high rate of gas flow and rapid cooling of the gaseous decomposition products. Under the best conditions and using the entire mercury arc spectrum, the yield of hydrazine was said to amount to 50 per cent of the ammonia decomposed.

Wiig and Kistiakowsky discounted the dissociation of ammonia into NH and H_2 , since such dissociation did not lead to a mechanism in agreement with the experimental results.²¹⁵ Nor did they believe their failure to observe hydrazine in the ammonia decomposition could be ascribed to its simultaneous photochemical decomposition.^{215a} They considered the likelihood of occurrence of each of the following secondary reactions.

- (1) $\text{H} + \text{H} + \text{M} \longrightarrow \text{H}_2 + \text{M}$
- (2) $\text{NH}_2 + \text{H} + \text{M} \longrightarrow \text{NH}_3 + \text{M}$
- (3) $\text{NH}_2 + \text{H}_2 \longrightarrow \text{NH}_3 + \text{H}$
- (4) $\text{NH}_2 + \text{H} \longrightarrow \text{NH}_3 + \text{H}_2$
- (5) $\text{NH}_2 + \text{NH}_2 + \text{M} \longrightarrow \text{N}_2\text{H}_4 + \text{M}$
- (6) $\text{NH}_2 + \text{NH}_2 \longrightarrow \text{N}_2 + 2\text{H}_2$
- (7) $\text{N}_2\text{H}_4 + \text{H} \longrightarrow \text{N}_2\text{H}_5 + \text{H}_2$
- (8) $\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2 \longrightarrow 2\text{NH}_3 + \text{N}_2$

²⁰⁹ Kassel, L. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 2495 (1927).

²¹⁰ Groth, W., *Z. physik. Chem.*, **37B**, 307 (1937).

²¹¹ Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); *J. Am. Chem. Soc.*, **49**, 1478 (1927).

²¹² Taylor, H. S., and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

²¹³ Koenig, A., and Brings, T., *Z. physik. Chem., Bodenstein-Band*, **541** (1931)

²¹⁴ Gedye, G. R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (1932).

²¹⁵ Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **54**, 1817 (1932).

^{215a} See in this connection, the discussion of the photochemical decomposition of hydrazine.

Triple collisions are probably not necessary in reactions (2) and (5).²¹⁶ At room temperature, (3) may be neglected as it implies a retardation of the rate of decomposition by hydrogen, an effect observable only at high temperatures. According to Boehm and Bonhoeffer,²¹⁷ (4) occurs extremely slowly. It may be that the increase in the quantum yield at high temperatures can be accounted for by this reaction, and that (3) also becomes effective under these conditions. Reactions (7) and (8) were set up to explain the absence of more than traces of hydrazine. The reaction at ordinary temperatures involves, according to Wiig and Kistiakowsky, reactions (1), (2), (5) and (7). The quantum yield on these assumptions would be

determined by the ratio k_2^2/k_1k_6 , this fraction being required to have a value of eight in order to account for a quantum yield of 0.25.

By using deuterium as an indicator, Taylor and Jungers²¹⁸ concluded that reaction (2) occurs to such an extent as to make it one of the reasons for the low quantum yield.²¹⁹ By irradiating mixtures of ammonia and deuterium, an equilibrium mixture of NHD_2 and NH_2D were obtained.

Studies of the concentrations²²⁰ of atomic hydrogen produced by the irradiation of ammonia showed that the yields were independent of the total pressure when the latter was varied from 250 to 760 mm. The atomic hydrogen was proportional to the 0.69 power of the absorbed light intensity, and passed through a maximum with increasing ammonia pressure. The effect of changing the temperature indicated that the reactions which destroy hydrogen atoms must have but an insignificant heat of activation. To account for their observations, they suggested that hydrogen atoms react with ammonia to form NH_4 molecules, decomposition of the latter at temperatures above 300°C . shifting the equilibrium to the left. At small ammonia pressures, the establishment of equilibrium was prevented by the diffusion of hydrogen atoms to the wall. Two reactions were accordingly suggested to account for the low quantum yield in the ammonia decomposition, $\text{NH}_4 + \text{NH}_2 \rightarrow 2\text{NH}_3$ and $\text{NH}_4 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{NH} + \text{H}_2$, the first being three hundred times as probable as the second. The rise of the quantum yield observed to occur at temperatures over 400°C . may be due to the above equilibrium moving so far to the left that not sufficient NH_4 remains to produce ammonia by either of these reactions.

Recently, the range of ammonia pressures over which the quantum yield is independent of the ammonia pressure has been extended to cover pressures of 1.2 to 8.5 atmospheres.²²¹ The yield is also independent of wave-length. The value found (0.14) was, however, lower than that of other investigators. A rather rapid increase of quantum yield with temperature was found, the values being 0.34 at 250°C and 0.54 at 400°C ., a result intermediate between those of Kuhn and of Wiig and Kistiakowsky. The method suggested for the disappearance of

²¹⁶ Mund, W., and van Tiggelen, A., *Bull. Soc. Chim. Belg.*, **46**, 104, 227 (1937), *Ann. Soc. Sci. Bruxelles, Ser. I*, **57**, 92 (1937); *Chem. Abs.*, **31**, 5685, 6560, 6971 (1937). These authors devise a mechanism which avoids reaction (2). See also Mund, W., Brenard, G., and Kaertkemeyer, L., *Bull. Soc. Chim. Belg.*, **46**, 211 (1937). For a further discussion of these relatively inaccessible papers, see Taylor, H. S., *J. Phys. Chem.*, **42**, 783 (1938).

²¹⁷ Boehm, E., and Bonhoeffer, K. F., *Z. physik. Chem.*, **119**, 385 (1926); Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

²¹⁸ Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

²¹⁹ A similar conclusion was reached by Melville, H. W., from work on the mercury sensitized reaction [*Trans. Faraday Soc.*, **28**, 885 (1932)].

²²⁰ Farkas, L., and Harteck, P., *Z. physik. Chem.*, **25B**, 257 (1934).

²²¹ Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **56**, 318 (1934).

hydrazine assumed the reactions $\text{H} + \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + \text{NH}_2$ and $2\text{NH}_2 + \text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$. The former was regarded as the more probable.²²² The decomposition of hydrazine was regarded as a photochemical process sensitized by ammonia.

Wiig²²³ finds that as the ammonia pressure is increased from zero the quantum yield at 2100Å rises from about 0.1 to a maximum of about 0.3 at 65 to 120 mm. pressure and then gradually falls off to about 0.18 at 840 mm. The average value is about that of Warburg, 0.25. The results agree with those of Ogg, Leighton and Bergstrom. It was also observed²²⁴ that the values depend to some extent upon the size of the reaction cell, decreasing in a cell of larger diameter. The reaction appears to become heterogeneous at ammonia pressures less than about 300 mm. and may be partly heterogeneous at higher pressures. Welge and Beckman²²⁵ detected the formation of hydrazine during the early stages of the reaction. The non-condensable portions of the gases had higher proportions of hydrogen than 75 per cent. At this early stage of decomposition, effected by the 1990Å line, the quantum yields averaged 0.87 and appeared to approach unity as a limit. The high quantum yields made it seem that recombination of the primarily formed NH_2 and H is not as important as had formerly appeared to be the case. A small amount of hydrazine may, however, be decomposed by hydrogen atoms with the formation of ammonia and nitrogen. The effect of the latter reaction becomes more exaggerated as the reaction proceeds.

During the early period of the investigation of the reaction of ammonia on irradiation considerable light was thrown upon it by studies on the mercury-sensitized reaction.²²⁶ It was, for example, in the case of the mercury-sensitized reaction that Taylor and Bates²²⁷ observed the reaction products to contain 89 per cent of hydrogen and 11 per cent of nitrogen, a circumstance which led to the development of mechanisms permitting the formation of hydrazine. Dickinson and Mitchell,²²⁸ who obtained 70 mole per cent of hydrogen, found the presence of argon and nitrogen at 0.3 mm. pressure had little effect on the reaction rate. On the other hand, hydrogen at 0.3 mm. and lower pressures had a large inhibiting effect, which increased with increasing ammonia pressures. Melville²²⁹ observed that in the presence of mercury vapor and hydrogen, the decomposition was less rapid when the ammonia was irradiated simultaneously by a mercury arc and a zinc spark than when irradiated by the zinc spark alone. The mercury resonance line dissociates the hydrogen. The resulting hydrogen atoms were believed to recombine with the NH_2 groups (formed by the predissociation of the ammonia by the zinc lines) more rapidly owing to the higher partial pressure of hydrogen atoms under these conditions. Gedye and Rideal²³⁰ found but little hydrazine produced in the mercury-sensitized reaction. The following mechanism is proposed by Welge and Beckman.²³¹

²²² See Dixon, J. K., *J. Am. Chem. Soc.*, **54**, 4262 (1932), and Wenner, R. R., and Beckman, A. O., *Ibid.*, **54**, 2787 (1932).

²²³ Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 1559 (1935).

²²⁴ Wiig, E. O., *J. Am. Chem. Soc.*, **59**, 827 (1937).

²²⁵ Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).

²²⁶ Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

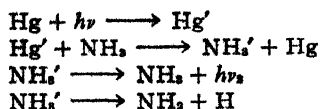
²²⁷ Taylor, H. S., and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

²²⁸ Dickinson, R. G., and Mitchell, A. C. G., *J. Am. Chem. Soc.*, **49**, 1478 (1927).

²²⁹ Melville, H. W., *Trans. Faraday Soc.*, **28**, 885 (1932).

²³⁰ Gedye, G. R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (1932).

²³¹ Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).



The low quantum yield of 0.12 was attributed to the occurrence of the fluorescence reaction.

Rate expressions were derived for this and the corresponding deuteroammonia (ND_3) reaction by Evans and Taylor.²³² Melville²³³ suggests that the decompositions are brought about in collisions between ammonia or ND_3 and metastable atoms. The metastable atoms are produced from quenching collisions between 3P_1 atoms and ammonia or ND_3 , the latter two being equally efficient. To account for the observed greater reactivity of ammonia, secondary reactions, unconnected with the mercury atom processes, were assumed. The quantum yield for the photo-sensitized reaction is about the same as that of the direct decomposition, so that the secondary reactions are the same.²³⁴

Berthelot and Gaudechon²³⁵ exposed mixtures of ammonia and oxygen to the total radiation of the mercury arc and found nitrogen, hydrogen and water, but no nitrates or nitrites, as products of the reaction. The reaction produced by the 2080A line of the zinc spark was more complex, according to Bacon and Duncan,²³⁶ since ammonium nitrate and smaller amounts of ammonium nitrite could be obtained. The process $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$ was assumed and the overall reaction could be written: $8\text{NH}_3 + 7\text{O}_2 \rightarrow 2\text{N}_2 + 2\text{NH}_4\text{NO}_3 + 8\text{H}_2\text{O}$.

The photochemical reaction of ammonia with carbon monoxide yields formamide as a primary product. The amide then undergoes secondary reactions.²³⁷ Less than 5 per cent of the reacting ammonia yields hydrogen and nitrogen. The rate of ammonia decomposition approximately doubles in the presence of carbon monoxide. Methylamine and ethylamine also react with carbon monoxide, a much larger amount of gaseous decomposition products being formed than in the reaction of ammonia.

The Photochemical Decomposition of Hydrazine. Faint diffuse absorption bands (apparently predissociation bands) begin at about 2490A in 80 cm. layers of hydrazine vapor at 0.5 mm. pressure.²³⁸ Continuous absorption begins at about 2370A (at 2260A in 20 cm. layers). Hilgendorff²³⁹ gives the heat of dissociation as 122.4 kcal. per mole.

Elgin and Taylor found that radiations shorter than 2400A decompose hydrazine by the reaction: $2\text{N}_2\text{H}_4 \rightarrow 2\text{NH}_3 + \text{N}_2 + \text{H}_2$, the ammonia subsequently decomposing at a rate about one-tenth that of the hydrazine decomposition rate. The hydrazine decomposition rate is independent of temperature, and of the addition of nitrogen, hydrogen or ammonia. The reaction can also be sensitized to the 2537A mercury line by the addition of mercury vapor; in this case the rate of the hydrazine decomposition so greatly exceeds that of the ammonia (40 times) that

²³² Evans, M. G., and Taylor, H. S., *J. Chem. Physics*, **2**, 732 (1934).

²³³ Melville, H. W., *Proc. Roy. Soc.*, **152A**, 325 (1935).

²³⁴ Farkas, L., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 621, 625 (1936); for the direct unsensitized decomposition of deuteroammonia, see Wigg, E. O., *J. Am. Chem. Soc.*, **59**, 955 (1937).

²³⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1327 (1910); see also Rakestraw, N. W., and Hollaender, A., *Science*, **84**, 442 (1936).

²³⁶ Bacon, H. E., and Duncan, A. B. F., *J. Am. Chem. Soc.*, **56**, 336 (1934).

²³⁷ Emeléus, H. J., *Trans. Faraday Soc.*, **28**, 89 (1932).

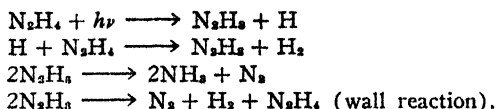
²³⁸ Elgin, J. C., and Taylor, H. S., *J. Am. Chem. Soc.*, **51**, 2059 (1929); see also Imanishi, M., *Nature*, **127**, 782 (1931).

²³⁹ Hilgendorff, H. J., *Z. Physik*, **95**, 781 (1935).

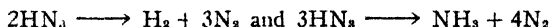
a nearly complete separation of the two reactions is possible. Indeed, it is the most rapid reaction obtained by means of excited mercury. The rate of the sensitized reaction is 110-120 times the rate of the direct photochemical decomposition. It is a chain reaction, the quantum yield being about 13. The rate of the sensitized reaction also is unaffected by nitrogen, ammonia or hydrogen added separately, although apparently the addition of both hydrogen and ammonia retards the reaction rate. The lack of retardation by hydrogen alone is explained by the assumption that hydrogen atoms react with hydrazine. The rate of the sensitized reaction is directly proportional to the incident light intensity.

The observed facts regarding the direct photochemical reaction could be explained by the assumption of a primary process leading either to a dissociation into N_2H_3 and H or into two NH_2 radicals.

The quantum yields produced by monochromatic light of 1990A, were found by Wenner and Beckman²⁴⁰ to range from 1.0 at a pressure of 2 mm. to 1.7 at 14 mm. The composition of the gases produced in the initial stages of the reaction was not in agreement with those reported by Elgin and Taylor. More hydrogen formed at the low hydrazine pressures than at the higher ones. The mechanism must differ from that of the mercury-sensitized reaction, because of the excess of hydrogen formed and because of the much lower quantum yield. Their suggested mechanism involved the reactions



The Decomposition of Hydrogen Azide. The ultraviolet irradiation of aqueous solutions of hydrogen azide yields mainly hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.²⁴¹ Gaseous hydrogen azide, on brief illumination with the 1990A line, gives a gas, non-condensable at liquid air temperatures; on longer illumination, a white solid, presumably ammonium azide, NH_4N_3 , is formed.²⁴² Light absorption by gaseous hydrogen azide sets in at 2200A. The decomposition proceeds by two concurrent reactions, one yielding hydrogen and nitrogen, and the other ammonia and nitrogen.



Over a pressure range of two to 130 mm., three molecules are decomposed per absorbed quantum, when calculated to the formation of ammonia. When sensitized by mercury vapor, there are also two concurrent reactions during the early part of the run, although their relative extents differ from those observed in the unsensitized reaction.

During the early period of the photosensitized reaction, the ammonia formed reacts with excess hydrogen azide to form solid ammonium azide. When the pressure has reached a value 1.18 times its initial value, excess hydrogen azide has all been consumed. After this, ammonia formed by the decomposition of ammonium azide remains as a gas and results in a sudden increase in the rate of change of total pressure. As the decomposition nears completion, a new reaction

²⁴⁰ Wenner, R. R., and Beckman, A. O., *J. Am. Chem. Soc.*, **54**, 2787 (1932).

²⁴¹ Glau, K., *Ber.*, **61**, 702 (1928).

²⁴² Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, **50**, 1870 (1928); **52**, 124 (1930); Myers, A. E., and Beckman, A. O., *Ibid.*, **57**, 89 (1935).

$\text{H}_2 + \text{HN}_3 \rightarrow \text{NH}_3 + \text{N}_2$ becomes increasingly important. When the pressure becomes constant no hydrogen remains, and the end products are given by $3\text{HN}_3 \rightarrow \text{NH}_3 + 4\text{N}_2$.

The quantum yield of the photosensitized reaction in its initial stage is 3.6; at pressures below 2 mm. the yield decreases rapidly. The value is in agreement with a calculated value of 3.4 molecules of HN_3 decomposed by either reaction per quantum absorbed, calculated to the formation of ammonium azide. The following possible partial reactions may be written:

- (1) $\text{Hg} + h\nu \longrightarrow \text{Hg}^*$
- (2) $\text{Hg}^* + \text{HN}_3 \longrightarrow \text{Hg} + \text{N}_2 + \text{HN}$
- (3) $\text{HN} + \text{HN}_3 \longrightarrow \text{H}_2 + 2\text{N}_2$
- (4) $\text{HN} + \text{HN}_3 \longrightarrow \text{N}_2 + \text{N}_2\text{H}_2$
- (5) $\text{N}_2\text{H}_2 + \text{HN}_3 \longrightarrow 2\text{N}_2 + \text{NH}_3$
- (6) $\text{NH}_2\text{HN}_3 \longrightarrow \text{NH}_4\text{N}_3 \text{ (solid).}$

18 per cent of the molecules react by (2) and (3) and 82 per cent by (2), (4), (5) and (6).

Reactions Involving the Oxides of Nitrogen. A direct combination of nitrogen and oxygen under the influence of rays from a quartz mercury arc occurs to a very slight extent.²⁴³ Kondrat'ev²⁴⁴ states that the amount of combination can be doubled by the addition of 5 per cent of hydrogen or of 28 per cent of carbon monoxide. The addition of both gases increases the yield ten times. It is assumed that excited oxygen molecules are involved in the combination process.

Nitrous Oxide. In the absorption spectrum of this gas there have been observed bands of nitric oxide. The presence of the latter is probably due to a photochemical decomposition occurring during the measurements.²⁴⁵ Sen-Gupta²⁴⁶ found that nitrous oxide absorbs light at 1850A, transmits better at about 1700A and absorbs again at 1580A. It was suggested that these absorptions represent dissociations into NO and nitrogen atoms in different metastable states. That produced by 1850A was said to be ^2D and that at 1580A ^2P . In each region the absorption is continuous.²⁴⁷ Absorption begins at longer wave-lengths as the temperature is increased (2246A at 20°C. and 2604 at 675°C.). By plotting the wave-length of beginning absorption against temperature and extrapolating to 0°, (2140A) it was deduced that the minimum energy required for the dissociation into NO and N is 132 kcal. From studies on mixtures of nitrogen peroxide with nitrous oxide, Henriques, Duncan and Noyes²⁴⁸ concluded that in the direct decomposition of the latter, a second primary process $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}$ is also necessary to explain the observed quantum yields.

Macdonald²⁴⁹ irradiated nitrous oxide at various pressures with radiations

²⁴³ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910). They found also that nitrous and nitric oxides are each decomposed into their elements, some of each gas reacting with liberated oxygen to form higher oxides.

²⁴⁴ Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

²⁴⁵ Lambrey, M., *Compt. rend.*, **186**, 1112 (1928).

²⁴⁶ Sen-Gupta, P. K., *Proc. Roy. Soc.*, **146A**, 824 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **3**, 197 (1934); *Chem. Abs.*, **29**, 7806 (1935).

²⁴⁷ Henry, L. A., *Compt. rend.*, **200**, 656 (1935); *J. chim. phys.*, **32**, 437 (1935). See also Dutta, A. K., *Proc. Roy. Soc.*, **138A**, 84 (1932).

²⁴⁸ Henriques, F. C., Jr., Duncan, A. B. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **6**, 518 (1938).

²⁴⁹ Macdonald, J. Y., *J. Chem. Soc.*, **1** (1928); cf. also Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **59**, 807 (1937).

(1860-1990A) from a condensed aluminum spark. The decomposition proceeded in accordance with the equation:



The quantum efficiency was 3.9 and was fairly independent of the pressure (21 to 607 mm.) and temperature (0° to 40°).

Excited mercury atoms can bring about the decomposition.²⁵⁰ In this case, nitrogen is liberated and the oxygen combines with the mercury, nitric oxide not being produced. The reaction velocity is proportional to the intensity of the 2537A line employed to excite the mercury.

A mercury-sensitized chain reaction between nitrous oxide and hydrogen has been studied by Melville.²⁵¹ Oxygen participates in both the making and breaking of the chains, the length of chains being approximately the same for the photochemical and the thermal reactions.

Nitric Oxide. Leifson²⁵² found an intense banded absorption to begin at 2264A. There are at least four groups of bands, which are interpreted as arising from combinations of four electronic levels with the ground state of the molecules.²⁵³ No regions of continuous absorption are apparent.

Macdonald²⁵⁴ found the decomposition produced by irradiating the gas with radiations of wave-lengths 1860-1990A to follow two courses. Ninety per cent of the decomposition yielded nitrogen and oxygen and 10 per cent followed the equation $3\text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2$. The quantum efficiency in this case is given as 0.73. The data were interpreted in terms of a theory of excited molecules serving as intermediaries, since the spectral data did not indicate the nature of the bands to be suggestive of predissociation.

On the other hand, Flory and Johnston²⁵⁵ have interpreted the primary process as one of predissociation, at least when the pressure was low (0.02 to 7 mm.). The final products of the reaction were found to be nitrogen and oxygen, the latter being partly destroyed by a reaction occurring when the gas was compressed in a McLeod gauge. In this process, a solid product presumably mercurous nitrate, was formed. It was shown that mercury²⁵⁶ vapor in the apparatus from the gauge did not essentially affect the results and that the reaction was at least 98 per cent non-sensitized since the use of a mercury vapor filter failed to reduce the rate of decomposition. The use of a Blue-Purple Corex A filter which cuts off the radiation completely below 2300A, but shows 70 per cent transmission of the 2537A line, reduced the rate to 1.3 per cent of its value without the filter. A similar experiment with a Cellophane filter cutting out radiation below 2200A and transmitting 45 per cent of that of the 2537A line reduced the rate to about 1 per cent of that without the filter.²⁵⁷

The rate of decomposition was directly proportional to the rate of absorption

²⁵⁰ Manning, W. M., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 3907 (1932).

²⁵¹ Melville, H. W., *Proc. Roy. Soc.*, **146A**, 737 (1934).

²⁵² Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926).

²⁵³ Sporer, H., and Hopfield, J. J., *Phys. Rev.*, **27**, 640 (1926); Jenkins, F. A., Barton, H. A., and Mulliken, R. S., *Phys. Rev.*, **30**, 150, 175 (1927); Lambrey, M., *Compt. rend.*, **186**, 1112 (1928); **187**, 210 (1928); **189**, 574 (1929); **190**, 261 (1930).

²⁵⁴ Macdonald, J. Y., *J. Chem. Soc.*, **1** (1928).

²⁵⁵ Flory, P., and Johnston, H., *J. Am. Chem. Soc.*, **57**, 2641 (1935).

²⁵⁶ Cf. also Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

²⁵⁷ Under other conditions, however, Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **53**, 514 (1931) found good evidence for the existence of a mercury-sensitized reaction. Under his conditions, there was no direct reaction. The differences in the manner of operation of the mercury arc source were, however, such that the results of these observers may not have been contradictory.

of the effective wave-lengths. At very low pressures, the rate was also directly proportional to the pressure, a circumstance which eliminated an excited molecule mechanism. Were the primary process of the latter type, the rate would vary as the square of the pressure since collisions with normal molecules would be required to effect a decomposition of the excited molecules. Most of the reaction produced by the mercury arc was attributed to absorption of the 1832A line by the *delta* band of nitric oxide. Absorption of the 1849A line in the *beta* band may have a lesser effect which becomes significant at higher pressures in agreement with the rates observed at pressures above 3 mm. Sparks between aluminum, zinc, cadmium, nickel, copper and tin electrodes were effective to the same order of magnitude. The activity of such sparks was regarded as due primarily to absorption in the continuous background. That the process is one of predissociation finds some support in the work of Kaplan²⁵⁸ on the emission bands of the gas. A calculated value for the molal heat of dissociation of nitric oxide, 121.95 kcal., is less than the energy of the 1830A line by 33.6 kcal. The dissociation products must, however, be normal atoms. The only secondary processes in the reaction are recombination processes occurring at the walls. It is suggested that at higher pressures the primary step may be predissociation from the upper levels of the *beta*-bands, rather than from the *delta*-bands.

Nitrogen Peroxide. At room temperatures this gas is composed of an equilibrium mixture of NO₂ and N₂O₄ molecules. The latter is non-absorbing in the visible range and the former is colored. Harris²⁵⁹ found the single molecules to exhibit a banded absorption spectrum between 6000 and 2250A. Lambrey²⁶⁰ tabulated the wave-lengths of the apparent absorption maxima and the individual intensities of the lines for the region 2083 to 4009A. The NO₂ molecule exhibits two limits of predissociation.²⁶¹ The first lies between 3800 and 3700A and the second between 2459 and 2200A. The diffuse bands of the first region extend to about 2596A, at which point they are suddenly replaced by a series of sharply defined bands probably coinciding with a different electronic transition. These bands then become diffuse at the second predissociation limit. The first limit corresponds to a dissociation into NO and a normal oxygen atom, the second to the production of an oxygen atom in the ¹D state.²⁶² The absorption attributed to the N₂O₄ molecules also present in the gas is continuous,²⁶³ consisting of two broad structureless bands at about 3400 and 2400A.²⁶⁴

On irradiation by means of the mercury arc, nitrogen peroxide was found by Norrish²⁶⁵ to exhibit a marked pressure increase. Since radiations transmitted by glass caused the pressure increase, the latter was attributed to a photochemical decomposition of the NO₂ molecules into nitric oxide and oxygen. The addition of either of these products completely reversed the reaction, nitric oxide being the more effective in displacing the equilibrium. The pressure increases rapidly at first, then slows down. The increase is complete in about fifteen minutes; when the illumination is stopped the pressure returns to its original value, rapidly at

²⁵⁸ Kaplan, J., *Phys. Rev.*, **37**, 1406 (1931).

²⁵⁹ Harris, L., *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

²⁶⁰ Lambrey, M., *Compt. rend.*, **188**, 251 (1929); see also Lambrey, M., and Corbière, J., *Compt. rend.*, **201**, 1334 (1935).

²⁶¹ Henri, V., *Nature*, **125**, 202 (1930).

²⁶² Mecke, R., *Z. physik. Chem.*, **7**, 127 (1930); Herzberg, G., *Z. physik. Chem.*, **10**, 189 (1930); Ionescu, A., *J. phys. radium*, **8**, 369 (1937).

²⁶³ See also Carwile, L., *Astrophys. J.*, **67**, 184 (1928).

²⁶⁴ Cf. Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

²⁶⁵ Norrish, R. W. G., *J. Chem. Soc.*, 761 (1927).

first and then more slowly. Constancy of pressure was attained when the rate of recombination of NO and oxygen became equal to the rate of the photodecomposition. Hydrogen had no effect on the increase of pressure. This work had been completed before the interpretation of the spectrum by Henri had appeared. Norrish, lacking this information, proposed a mechanism involving a reaction between an excited and a normal molecule of NO_2 in which molecular oxygen was produced.

By a method insuring only very low partial pressures of the reaction products, Dickinson and Baxter²⁶⁶ were able to avoid the recombination of the products and the resulting heat effect. Under their conditions, it was not necessary to treat the reaction as an equilibrium and quantum yields could be determined for the direct decomposition. The yields were determined in a series of spectral regions, isolated by the use of filters. The following mean values, expressed as molecules of oxygen per quantum absorbed, were obtained: 4350A, 0.0046; 4050A, 0.036; 3660A, 0.77. At the low pressures used, the values were not markedly dependent on the pressure.

These observations were extended by Norrish²⁶⁷ to include six wave-lengths. The yield was zero at 5760, 5460 and 4360A. For 4050A, it was 0.37, at 3650A 1.05 and for the range 3160 to 2650A, 1.04. It is particularly interesting that a photochemical threshold is found in the middle of a region in which the substrate absorbs strongly, the maximum absorption of nitrogen peroxide being at about 4500A where the quantum yield is zero. Light of the photochemically inactive wave-length 4360A produced an orange fluorescence and the violet light of 4050A, which is only partly effective photochemically, a much fainter greenish-yellow fluorescence. The spectra of the fluorescence at each wave-length possessed two wide maxima at about 6400 and 5900A, different intensity distributions accounting for the difference in color. At 3650A only a very faint fluorescence could be produced. When present, the fluorescence could be destroyed by the addition of oxygen. These observations can now be interpreted as evidence that predissociation begins at about the threshold region, necessitating a revision of previously assumed excited molecule mechanisms.

The presence of nitrogen pentoxide does not affect the decomposition of the nitrogen peroxide, according to Holmes and Daniels.²⁶⁸ Their quantum yields, based on molecules of NO_2 decomposed, in a mixture of the above gases were 1.92 at 3130A, 1.83 at 3660A, 0.5 at 4050A and zero at 4360A. They also found that N_2O_4 is decomposed at 2650A with a quantum efficiency of 0.6. Although the lines 3660 and 3130A are absorbed by this gas, no measurable decomposition results. Helium, argon, nitrogen, oxygen, hydrogen, carbon dioxide and nitrous oxide were found to decrease the photolysis of NO_2 , but were more effective in reducing fluorescence.

The synthesis of nitrogen dioxide in a glow discharge in a two to one oxygen:nitrogen mixture has been reported by Westhaver and Brewer.²⁶⁹

Nitrogen Pentoxide. The absorption of this gas, according to Urey, Dawsey and Rice²⁷⁰ is continuous from 3050A into the Schumann region. The upper

²⁶⁶ Dickinson, R. G., and Baxter, W. P., *J. Am. Chem. Soc.*, **50**, 774 (1928).

²⁶⁷ Norrish, R. W. G., *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

²⁶⁸ Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

²⁶⁹ Westhaver, J. W., and Brewer, A. K., *J. Phys. Chem.*, **34**, 554 (1930).

²⁷⁰ Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 3190 (1929). See also Jones, E. J., and Wulf, O. R., *J. Chem. Phys.*, **3**, 873 (1938).

absorption limit corresponds with an energy of 93.2 kcal, suggesting that the primary reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}$ occurs.

Holmes and Daniels,²⁷¹ who also gave absorption data, stated that light of wave-lengths 2800 and 2650Å decomposes the pentoxide with a quantum efficiency of 0.6.

Nitrogen pentoxide is also decomposed photochemically by blue light, but only in the presence of nitrogen peroxide as a sensitizer.²⁷² Light in the region 4000 to 4600Å is responsible for the reaction, the rate being proportional to the energy absorbed by the nitrogen peroxide. At low concentrations of the sensitizer, the rate is proportional to the amount present. From the data given, Kistiakowsky²⁷³ has calculated an upper quantum yield limit of about 18.

Fazel and Karrer²⁷⁴ suggested that the excited nitrogen peroxide molecules transferred their energy by collisions of the second kind to molecules of nitrogen pentoxide, thereby dissociating the latter. Norrish,²⁷⁵ however, suggested that the nitrogen peroxide might be decomposed, the resulting nitric oxide molecules then reacting with nitrogen pentoxide with the production of three molecules of nitrogen peroxide, the original sensitizer. Busse and Daniels²⁷⁶ found the rate of this photosensitized reaction to be unaffected by collisions with oxygen, nitrogen or hydrogen. Bromine could not be substituted for the nitrogen peroxide even though the halogen has a rather similar absorption range. When added to a mixture containing nitrogen peroxide, bromine decreases the sensitizing efficiency of the latter, probably by absorbing a portion of the effective light. From measurements of the relative rates of decomposition of nitrogen pentoxide at 0°C. by radiations of wave-lengths 4350, 4050 and 3660Å, and comparison with the data on the decomposition of nitrogen dioxide, Baxter and Dickinson²⁷⁷ concluded the mechanism of the sensitized nitrogen pentoxide decomposition to be essentially that suggested by Norrish.

Nitrosyl Chloride. Magnanini²⁷⁸ found nitrosyl chloride to exhibit weak absorption bands in the region 5300-6200Å; strong absorption sets in at 5300Å. Kistiakowsky²⁷⁹ states that the absorption begins above 6300Å and increases gradually toward the ultraviolet. In the region between 5100 and 4350Å the banded structure showed faint but diffuse line structure. In the ultraviolet below the absorption maximum at 3300Å no banded structure could be observed at all.

According to Kiss²⁸⁰ visible light decomposes nitrosyl chloride incompletely into nitric oxide and chlorine, which recombine in the dark, a stationary state being finally reached. The temperature coefficient is unity (0° to 78°C.). Working with the spectral regions 4380-5000 and 4480-5200Å, isolated by means of filters, Bowen and Sharp²⁸¹ found the quantum yield to be 0.5 independent of the extent of the decomposition. Their proposed mechanism included a primary dissociation into nitric oxide and a chlorine atom, followed by some secondary reactions in which the chlorine atom produced the transitory compound NOCl_2 . Quite different

²⁷¹ Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

²⁷² Daniels, F., and Johnston, E. H., *J. Am. Chem. Soc.*, **43**, 72 (1921).

²⁷³ Kistiakowsky, G. B., "Photochemical Processes," The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), New York, 1928, 140.

²⁷⁴ Fazel, C. S. and Karrer, S., *J. Am. Chem. Soc.*, **48**, 2837 (1926).

²⁷⁵ Norrish, R. W. G., *Nature*, **119**, 123 (1927).

²⁷⁶ Busse, W. F., and Daniels, F., *J. Am. Chem. Soc.*, **49**, 1257 (1927).

²⁷⁷ Baxter, W. P., and Dickinson, R. G., *J. Am. Chem. Soc.*, **51**, 109 (1929).

²⁷⁸ Magnanini, G., *Z. physik. Chem.*, **4**, 427 (1889).

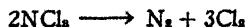
²⁷⁹ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **52**, 102 (1930).

²⁸⁰ Kiss, A., *Rec. trav. chim.*, **42**, 665 (1923).

²⁸¹ Bowen, E. J., and Sharp, J. F., *J. Chem. Soc.*, **127**, 1026 (1925).

results were reported by Kistiakowsky,²⁸² who obtained a quantum yield of 2.1 at each of several wave-lengths from 6350 to 4350A, and probably also at 3650A. No explanation could be given for the divergence from the results of Bowen and Sharp. Kistiakowsky also believed the spectral evidence favored an interpretation by means of excited nitrosyl chloride molecules rather than one of direct dissociation for the primary process.

Nitrogen Trichloride. The decomposition of nitrogen trichloride



is sensitized by chlorine, the velocity being directly proportional to the light absorbed by the added chlorine.²⁸³

The reaction is of zero order with respect to nitrogen trichloride until the decomposition is practically complete; a semi-explosive reaction then occurs. With pressures of nitrogen trichloride of 0.146 to 2.48 mm. and of chlorine between 100 and 22 mm. the quantum efficiencies (at 4360 and 3650A) were high, between 17 and 5, depending on the pressure of the chlorine. They tended to approach a limiting value of about three at the highest pressures of chlorine. If the vessel is treated with water or heated to 100°C., the efficiency is abnormally high; the "maturing" of a vessel is chiefly the formation of an invisible film of ammonium chloride on the surface which indirectly establishes a constant condition of chain rupture in the gas phase. The relation between the yield and the chlorine pressure is given by

$$\frac{1}{0.0038P_{\text{Cl}_2}} = K_1$$

in which K_1 varies from 2.0 to 2.5 and is dependent on the size of the vessel. Foreign gases reduce the quantum yield to a limiting value of two, the relation being

$$\frac{1}{(0.0038P_{\text{Cl}_2} + K_2P_{\text{gas}})} = 2.5.$$

The K_2 values were: helium 0.00093, argon 0.0016, nitrogen 0.0017, oxygen 0.0025 and carbon dioxide 0.0038. It was suggested that the added gas stabilizes by triple collisions an energy-rich complex, NCl_4 , which is associated with the rupture of chains.

THE PHOTOCHEMISTRY OF SULFUR COMPOUNDS

The gaseous reaction between hydrogen and sulfur is greatly aided by the ultraviolet rays from a mercury vapor lamp, according to Norrish and Rideal.²⁸⁴ The absorption spectrum of sulfur vapor contains a band with maximum absorption at 2750A according to Graham.²⁸⁵ It is known that this value lies within one of the two predissociation regions possessed by sulfur vapor.²⁸⁶

The absorption of hydrogen sulfide, which is entirely continuous, begins at about 2800A and reaches a maximum at about 1850A.²⁸⁷ The gas can be decom-

²⁸² Kistiakowsky, G. B., *loc. cit.*

²⁸³ Griffiths, J. G. A., and Norrish, R. W. G., *Proc. Roy. Soc.*, **130A**, 591 (1931); **135A**, 69 (1932).

²⁸⁴ Norrish, R. W. G., and Rideal, E. K., *J. Chem. Soc.*, **125**, 2070 (1924); **123**, 3202 (1923).

²⁸⁵ Graham, J. I., *J. Chem. Soc.*, **98** (ii), 1015 (1910).

²⁸⁶ Christy, A., and Naudé, S. M., *Phys. Rev.*, **37**, 903 (1931).

²⁸⁷ Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27**, 395 (1931).

posed by the light of the mercury arc²⁸⁸ or of the zinc spark. Using the latter source, Stein²⁸⁹ found the quantum yield to be 2 (2050Å) when the hydrogen sulfide pressure was 250 mm. At higher pressures the quantum yield reached 3.8. The nature of the primary process was not determined. On the other hand, Forbes, Cline and Bradshaw²⁹⁰ find the yield to be unity and independent of pressure between 8 and 1400 mm. and of light flux over a 14-fold range at 2080Å.

The Oxides of Sulfur. Sulfur monoxide, spectral evidence for the existence of which has been presented by Henri and Wolff,²⁹¹ is said to undergo a photochemical decomposition when irradiated by the shorter ultraviolet wave-lengths.²⁹² A slight contraction in volume of sulfur dioxide was observed by Berthelot and Gaudechon²⁹³ to occur in a sample of the gas irradiated over a mercury surface. Sulfur was deposited on the tube and the mercury became encrusted with a sulfate. Corresponding results were also obtained in the presence of oxygen. Similar observations have been reported by Hill,²⁹⁴ who used a Uviol mercury lamp. He represented the decomposition as $3\text{SO}_2 \rightarrow 2\text{SO}_3 + \text{S}$. By interposing various filters it was found that the chief response is at 3130Å, lying within the first absorption band of sulfur dioxide. The gas has a well-developed band system which extends from about 3400Å to shorter wave-lengths.²⁹⁵ Predissociation into SO and O sets in at about 1950-1900Å. Predissociation also is possible at about 2100Å.²⁹⁶

Kornfeld and McCaig²⁹⁷ obtained the absorption spectrum of sulfur dioxide before and after it had been irradiated at low temperatures with an aluminum spark.

Although the gas decomposes at these wave-lengths into SO and O, the spectrum of SO was not observed. Because of its surplus vibrational energy, the latter was possibly consumed in an unexpectedly rapid reaction.

The spectrum of sulfur trioxide shows continuous absorption from 3300 to 2600Å and from 2300 to 2000Å.²⁹⁸ Kornfeld²⁹⁹ concludes that at 2760Å dissociation produces SO_2 and a normal state oxygen atom.

Konstantinova-Shlezinger³⁰⁰ states that the sulfur trioxide produced when sulfur dioxide is irradiated in a quartz vessel, is decomposed to some extent by the reaction $2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$.

The Oxidation of Sulfur Dioxide. Coehn and Becker³⁰¹ found that the formation of sulfur trioxide proceeds fairly rapidly in a mixture of sulfur dioxide and oxygen in a quartz reaction vessel mounted within a mercury lamp. With a mixture of equal volumes of sulfur dioxide and oxygen, the content of sulfur trioxide was 65 per cent at equilibrium. The latter condition was attained within an hour at a temperature of 160°C. This is quite different from the thermal equilibrium, since in daylight at temperatures below 450°C., there is practically 100 per

²⁸⁸ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).

²⁸⁹ Stein, N. O., *Trans. Faraday Soc.*, **29**, 583 (1933).

²⁹⁰ Forbes, G. S., Cline, J. E., and Bradshaw, B. C., *J. Am. Chem. Soc.*, **60**, 1431 (1938).

²⁹¹ Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929).

²⁹² Cordes, H., and Schenk, P. W., *Trans. Faraday Soc.*, **30**, 31 (1934).

²⁹³ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).

²⁹⁴ Hill, R. A., *Trans. Faraday Soc.*, **20**, 107 (1924); see also Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).

²⁹⁵ Watson, W. W., and Parker, A. E., *Phys. Rev.*, **37**, 1484 (1931); Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929); Chow, T.-C., *Phys. Rev.*, **44**, 638 (1933); Wieland, K., *Nature*, **130**, 847 (1932); *Trans. Faraday Soc.*, **30**, 260 (1934).

²⁹⁶ Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

²⁹⁷ Kornfeld, G., and McCaig, F., *Trans. Faraday Soc.*, **30**, 991 (1934); *Chem. Abs.*, **29**, 680 (1935).

²⁹⁸ Dutta, A. H., *Proc. Roy. Soc.*, **137A**, 366 (1932).

²⁹⁹ Kornfeld, G., *Trans. Faraday Soc.*, **33**, 614 (1937).

cent sulfur trioxide at equilibrium. The irradiation equilibrium was found not to be displaced by increases of temperature up to 800°C., whereas the dark equilibrium is displaced considerably when the temperature is raised above 450°C. The temperature coefficient of the oxidation rate was found to be 1.2. These authors also made experiments with flowing systems at temperature of 450°C. and obtained yields so high as to lead them to believe a technical process for the production of sulfuric acid to be feasible.³⁰²

In a repetition of this work, Trautz and Helfrich³⁰³ found the mass law to hold within the limit of experimental error, and observed the equilibrium constant to vary linearly with the square of the current to the mercury arc. The introduction of argon or nitrogen had no effect on the equilibrium constant. They also claimed that completely dried sulfur dioxide neither decomposed when irradiated nor was oxidized in the presence of oxygen.

The quantum yields have been determined for a series of wave-lengths of monochromatic light by Kornfeld and Weegmann.³⁰⁴ At 2537Å and longer wave-lengths, the yield was less than 0.01, and even this was decreased by increasing the concentration of sulfur trioxide. The yields were 0.53 at 2200Å, 0.71 at 2070Å and 1.0 at 1806Å. They attributed the results to a mechanism involving dissociation. The slight yields at the longer wave-lengths were said to be explained by a different mechanism since there is insufficient energy for dissociation. Franck, Spomer and Teller³⁰⁵ considered the process of oxidation to involve excited molecules of sulfur dioxide. Beyond 1950Å, in the predissociation region, they found the quantum yield to rise to three.

Sulfuryl Chloride. The absorption by this material is continuous at wave-lengths less than 2600Å.³⁰⁶ LeBlanc, Andrich and Kangro³⁰⁷ stated the absorption to begin at 3000Å and to rise rapidly at shorter wave-lengths. With radiations absorbed by sulfuryl chloride, but not to a marked extent by either sulfur dioxide or chlorine, there is practically complete dissociation either at 55°C. or at 100°C. These authors believed that irradiation of mixtures of sulfur dioxide and chlorine by wave-lengths absorbed by the former caused only slight changes which did not result in the formation of sulfuryl chloride. On the other hand, radiations absorbed by the chlorine caused the reaction to run to an equilibrium, the position of which depended on the temperature and the amount of moisture present.

Trautz³⁰⁸ found that the radiations about 2900Å caused the combination of the two gases to proceed smoothly as a second order reaction, particularly at higher temperatures. Sulfuryl chloride was not the only product of the reaction; if relatively short periods of exposure were separated by several hours of darkness, other substances formed and decreased the velocity constant. When continuous irradiation was employed, constants were no longer obtained, probably on account of the side reactions. A temperature increase of 80°C. decreased the velocity of the

³⁰⁰ Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).

³⁰¹ Coehn, A., and Becker, H., *Z. physik. Chem.*, **70**, 88 (1910).

³⁰² Coehn, A., and Becker, H., *German P.* 217,772, July 9, 1907.

³⁰³ Trautz, M., and Helfrich, F., *Z. wiss. Phot.*, **33**, 72, 111, 117 (1934); *Brit. Chem. Abs. A*, **975**, 1183 (1934).

³⁰⁴ Kornfeld, G., and Weegmann, E., *Z. Elektrochem.*, **36**, 789 (1930).

³⁰⁵ Franck, J., Spomer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

³⁰⁶ Asundi, R. K., and Samuel, R., *Current Sci.*, **3**, 417 (1935); *Chem. Abs.*, **29**, 3914 (1935).

³⁰⁷ LeBlanc, M., Andrich, K., and Kangro, W., *Z. Elektrochem.*, **25**, 229 (1919); *Chem. Abs.*, **14**, 493 (1920).

³⁰⁸ Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).

combination, corresponding to a temperature coefficient of 0.88 per 10°C. The velocity of the formation reaction is of the same order as that which is catalyzed by animal charcoal in the dark, whether Uviol light or that from a quartz lamp is used.

Attempts to obtain sulfuryl bromide by the irradiation of sulfur dioxide and bromine have not been successful.³⁰⁹

PHOTOCHEMISTRY OF MISCELLANEOUS SUBSTANCES

Phosphine and Arsine. In the absorption spectrum of phosphine, Cheesman and Emeléus³¹⁰ observed poorly developed bands with centers at approximately 2315 and 2290Å. Arsine and stibine showed only continuous absorption. In the photochemical decomposition of the latter, hydrogen was formed.

The mercury-sensitized decomposition of phosphine, as affected by variations in the partial pressures of phosphine, hydrogen, oxygen and argon, was investigated by Melville.³¹¹ Collision of excited mercury atoms with phosphine was believed to produce H and PH₂. Recombination of these products by a wall reaction was indicated by the decrease in the reaction rate which was observed to follow an increase in the surface-to-volume ratio of the vessel. An observed inhibition by added hydrogen was attributed to the effect of the latter in deactivating the excited mercury atoms and to a wall reaction between the additional atomic hydrogen so produced and the phosphorus-containing intermediate. By attacking the intermediate, added oxygen increased the rate of the phosphine decomposition. That the oxide so formed initiated a stable chain reaction between the remaining phosphine and oxygen was shown by the acceleration of this reaction by argon.

The lowering of the explosion limit of phosphine-oxygen mixtures by mercury arc irradiation was shown to be due to a surface effect probably connected with the adsorption of hydrogen by the wall of the containing vessel. The direct photochemical decomposition of phosphine by the radiations from zinc or aluminum sparks leads to the formation of hydrogen and red phosphorus.³¹²

Melville³¹³ also finds that at room temperature the absorption spectrum of phosphine consists of a region of continuous absorption beginning at 2300Å, preceded by four diffuse bands. At 300°C., the bands disappear and the absorption limit moves toward longer wave-lengths. The direct photochemical decomposition has a quantum yield of 0.56 when conducted in a 7 cm. bulb and 0.49 in a 2 cm. bulb. It is independent of temperature below 300°. Atomic, but not molecular, hydrogen decreases the yield.

An oxygen-phosphine mixture reacts explosively between two sharply defined pressure limits. The lower one can be diminished by irradiation between the wave-lengths of 2500 and 2800Å. The effect is ascribed to the formation of a small quantity of an active substance from the phosphine; this does not decay immediately when the elimination ceases.³¹⁴

Melville and Roxburgh³¹⁵ found for the reaction produced by irradiation of

³⁰⁹ Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915); Schwarz, R., and Kunzer, W., *Z. anal. Chem.*, **183**, 376 (1929).

³¹⁰ Cheesman, G. H., and Emeléus, H. J., *J. Chem. Soc.*, 2847 (1932).

³¹¹ Melville, H. W., *Proc. Roy. Soc.*, **138A**, 374 (1932).

³¹² Melville, H. W., *Nature*, **129**, 546 (1932).

³¹³ Melville, H. W., *Proc. Roy. Soc.*, **139A**, 541 (1933); Melville, H. W., and Bolland, J. L., [*Ibid.*, **160A**, 384 (1937)] and Melville, H. W., Bolland, J. L., and Roxburgh, L., [*Ibid.*, 406] also investigated mercury-sensitized exchange reactions of deuterium and phosphine and the decomposition of tri-deuterophosphine.

³¹⁴ Hinshelwood, C. N., and Clusius, K., *Proc. Roy. Soc.*, **129A**, 589 (1930).

³¹⁵ Melville, H. W., and Roxburgh, L. H., *J. Chem. Physics*, **2**, 739 (1934).

an oxygen-phosphine mixture at 0.05 mm. a quantum yield of 200, a stable chain reaction occurring. Above the upper limit of irradiation for explosion in the photochemical oxidation of phosphine, the chain reaction is inhibited by oxygen.

Since the continuous absorption of arsine begins at only 2390Å, the sensitized decomposition produced by mercury atoms excited by the 2537Å line may be studied without any complication due to a direct reaction.³¹⁶ Hydrogen gas and a film of arsenic are formed. The rate of decomposition is directly proportional to the intensity of the light and, at high pressures, is independent of the arsine pressure. At low pressures, the rate is decreased because the excited mercury atoms lose some of their energy by fluorescence. The decomposition is very slightly inhibited by addition of hydrogen. The quantum yield is 1.03.

Germane absorbs only in the very short wave-length region, probably at about 1700Å. Absorption is entirely continuous at least as far as 1550Å.³¹⁷ Radiations transmitted by very thin layers of quartz will decompose germane into hydrogen and germanium. The primary process is uncertain. A mercury-sensitized reaction also leads to the same products.³¹⁸

A mercury-sensitized decomposition of silane to hydrogen and a solid SiH_x has been reported by Emeléus and Stewart.³¹⁹ The lack of absorption by this material prevents the occurrence of any direct photochemical decomposition. Mixtures of 30-50 per cent of silane with oxygen at low pressures explode when irradiated by the mercury resonance line, hot mercury spark, or aluminum spark. The process may be due to the formation of excited oxygen molecules. At higher pressures (100-500 mm.), the mixture reacts slowly after an induction period which depends on the initial pressure and oxygen concentration to give silicon. At the beginning the pressure increase is an exponential function of the time.

Siloxene, $\text{Si}_6\text{O}_3\text{H}_8$, reacts with organic halides in the presence of light to produce a monohalogenated siloxene.³²⁰ Siloxene absorbs only light of short wave-length, but can be sensitized to long wave-lengths by the addition of a very small quantity of hydroxysiloxene or of a dye. Since colored products are formed as the reaction proceeds, there is also autosen sensitization.

Iron pentacarbonyl vapor can be decomposed by irradiation with the wave-length 4000Å, with a quantum efficiency of two.³²¹ The reaction is inhibited by foreign gases. Eyber explained the results by assuming an excited molecule to react with a normal one with the production of carbon monoxide and the compound $\text{Fe}_2(\text{CO})_9$. On the other hand, Thompson and Garratt³²² found the vapor to have continuous absorption beginning at 4100Å. They suggested that the primary process involves a dissociation into CO and $\text{Fe}(\text{CO})_4$. The latter then reacts with a molecule of the pentacarbonyl to give the observed product $\text{Fe}_2(\text{CO})_9$. In hexane or carbon tetrachloride the continuum began at 5500Å, but this was attributed to the presence of the decomposition product as an impurity. Eyber found that hexane solutions absorb strongly below about 4600Å.

Both the vapor and hexane or carbon tetrachloride solutions of nickel tetracarbonyl show only continuous absorption, beginning at 3950Å. The first reaction

³¹⁶ Simmons, N. L., and Beckman, A., *J. Am. Chem. Soc.*, **58**, 454 (1936).

³¹⁷ Mahncke, H. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **57**, 456 (1935).

³¹⁸ Romeyn, H., Jr., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 4143 (1932).

³¹⁹ Emeléus, H. J., and Stewart, K., *Trans. Faraday Soc.*, **32**, 1577 (1936). x is < 0.9 . For disilane and trisilane decomposition, see Schwarz, R., and Heinrich, F., *Z. anorg. allgem. Chem.*, **221**, 277 (1935).

³²⁰ Kautsky, H., and Thiele, H., *Z. anorg. allgem. Chem.*, **144**, 197 (1925); *Chem. Abs.*, **19**, 2313 (1925).

³²¹ Eyber, G., *Z. physik. Chem.*, **144A**; see also Warburg, O., *Naturwiss.*, **16**, 856 (1928).

³²² Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 525 (1934).

of irradiation is to produce carbon monoxide and nickel tricarbonyl, the latter further dissociating into carbon monoxide and nickel. In the gas phase, however, no change is observed,⁸²³ a thermal recombination balancing the photochemical decomposition. The quantum efficiency is higher, 2.12, for solutions in carbon tetrachloride than for those in hexane or cyclohexane. The yield increases somewhat with frequency from a threshold value corresponding to the limit of continuous absorption. Fedorov and Talmud⁸²⁴ find the reaction can be sensitized to wave-lengths greater than 6400A by pinacyanol. Webster⁸²⁵ claims the polymerization of nickel carbonyl to $(\text{Ni}(\text{CO})_4)_2$, which has antiknock properties when added to motor fuels, by the action of actinic light.

⁸²³ Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 1817 (1934).

⁸²⁴ Fedorov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, 8, 789 (1936); *Chem. Abs.*, 31, 1702 (1937).

⁸²⁵ Webster, H. G., U. S. P. 2,002,805, May 28, 1935; *Chem. Abs.*, 29, 4932 (1935).

Chapter 20

Inorganic Reactions in Liquids

GENERAL CHARACTERISTICS

In liquid phase reactions the photochemical mechanism may be altered because of the influence of neighboring molecules of the reactant if a pure liquid, or of the solvent if a solution, upon the molecule which absorbs a photon. These influences are exerted even during the act of absorption. As pointed out by Franck and Rabinowitsch,¹ the molecules in a liquid may be regarded as being permanently in a state of collision. As a result, collisions with adjacent molecules are occurring during the brief period between the absorption of a photon by a molecule and its dissociation (about 10^{-18} second). Such collisions may deactivate the excited molecule even before it has a chance to dissociate. Accordingly, the yield of the primary process might be expected to fall below unity. A lowered quantum yield in the primary process would be reflected also in a lowered quantum yield for the measured overall reaction. This consideration would apply to any photochemical process in which the primary act is the formation of an excited molecule.

Since all collisions between dissociation products would be triple collisions with solvent molecules, the occurrence of secondary recombination processes would be enhanced and contribute to a lowering of the quantum yield. Such processes would be true recombinations of the dissociation products of individual molecules rather than combinations of products of dissociation of different molecules or of products produced in secondary reactions. This follows because any excess kinetic energy with which atoms or free radicals may be endowed, by virtue of a dissociating photon of slightly shorter wave-length than corresponds to the energy required for dissociation, would be lost by collision before the products had moved much more than a molecular diameter. Recombination would then be possible if the products were still close together. When much shorter wave-lengths are used in irradiation, the kinetic energies of the dissociation products are great, enabling the latter to travel farther apart before losing this excess energy. The result would be a reduction of the chance of recombination and an increase in the quantum yield over that produced by the use of longer wave-lengths.²

In certain liquids and in solutions in non-polar solvents such as carbon tetrachloride, it is possible that the rates and temperature coefficients of secondary processes are not far different from those in the gaseous state.³ In other cases there may be complications due to combinations of the solvent with the dissociation products of the primary process. Indeed, the original solute may be solvated

¹ Franck, J., and Rabinowitsch, E., *Trans. Faraday Soc.*, **30**, 129 (1934).

² Sveshnikov, B. Y., [*Acta Physicochim. U.R.S.S.*, **3**, 257 (1935)] has discussed the theory of the quenching of the fluorescence of excited molecules as dependent on the viscosity of the solvent. He has also considered the effect the concentration of a reactant which does not require activation may have on the mean life of excited molecules. *Compt. rend. acad. sci. U.R.S.S.*, **15**, 177 (1937); *Chem. Abs.*, **31**, 656 (1938). Note also Schpoliski, E., *Acta Physicochim. U.R.S.S.*, **3**, 255 (1935).

³ Moelwyn-Hughes, E. A., "Kinetics of Reactions in Solution," p. 63. Oxford University Press, 1933.

and give rise to further complications. Details of effects exerted by the solvent upon secondary processes will be discussed in connection with individual reactions.

Dickinson⁴ pointed out that as a result of these possibilities, reactions in the liquid phase might be expected to have quantum yields less than, or in some cases equal to but never greater than, those of the same reactions in the gas phase. He examined the reactions in which available data permitted a comparison of the yields in the two states. Of eleven reactions studied, ten exhibited yields in the liquid phase which were slightly less than those in the gas phase. An exception was the decomposition of ethyl iodide produced by absorption within the continuous spectral region. This halide, according to West and Ginsburg,⁵ undergoes little decomposition in the gas phase and more in the liquid phase or in solution in hexane or benzene. Dickinson, however, raised the question as to whether the effects of traces of oxygen had been entirely eliminated in this work.⁶

Rollefson⁷ has discussed cases in which the solute is affected by the solvent and, in particular, the influence of the solvent, especially if polar, upon photosensitization processes effected by such fluorescent substances as uranyl salts.

Absorption Spectra. Spectral evidence as to the nature of the primary process—dissociation, predissociation or formation of excited molecules—is rarely available for the interpretation of photochemical reactions in condensed systems. However, the products capable of secondary reactions will be dissociation products, for collisions would easily lead to the dissociation of excited molecules. The absorption spectra of liquids seldom exhibit the fine structure characteristic of transitions between rotational levels of molecules seen in the absorption of gases and the occurrence of which was used as a criterion of the absence of predissociation. Even the more widely separated bands characterizing the vibrational levels of molecules are usually but partially distinguishable. The blurring of the finer structure is in part attributable to the effect of collisions with neighboring molecules and in part to the Stark effect of the charges of the adjacent molecules. The effects of collision-broadening may be lessened by making the observations at liquid air temperatures in some cases. This is particularly to be observed in the case of crystals. For example, at very low temperatures (20°Abs.) sharp lines replace the broad absorption bands of potassium dichromate observable at ordinary temperatures.⁸

In other cases, as azobenzene, the broad bands seen at ordinary temperatures are broken into a series of narrow but still diffuse bands at -196°C., forming a line spectrum at 20°Abs.

Aside from the obliteration of the finer structure, the situation of the absorption region may be either unaffected or shifted to other wave-lengths by the presence of a solvent. Instances in which there is similarity in absorption in the gas phase and in liquid solution are found in the halogens as vapors or in solution in carbon tetrachloride, chloroform or carbon disulfide, and for hydrogen sulfide in water and in hexane. When the solute is solvated, there may, however, be

⁴ Dickinson, R. G., *Chem. Rev.*, **17**, 413 (1935); *J. Phys. Chem.*, **42**, 739 (1938); see also Rollefson, G. K., and Libby, W. F., *J. Chem. Physics*, **5**, 569 (1937).

⁵ West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56**, 2626 (1934).

⁶ For further discussion of the modifications of the quantum yield of the primary process which may occur in solution, see also Kistiakowsky, G. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 44 (1935), and Rabinowitch, E., and Wood, W., *Trans. Faraday Soc.*, **32**, 1381 (1936).

⁷ Rollefson, G. K., *Chem. Rev.*, **17**, 425 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 19 (1935); *Chem. Abs.*, **30**, 6648 (1936).

⁸ Obreimow, I., and de Haas, W. J., *Proc. K. Acad. Wetensch. Amsterdam*, **31**, 353 (1928); Schumann, H., *Z. Physik*, **76**, 106 (1932).

marked shifts in the situation and intensity of the absorption bands.⁹ The effects of variation of temperature on the extinction coefficients of a number of salt solutions, mostly colored, have been measured by Mukerji, Bhattacharji and Dhar.¹⁰ The changes are in large part attributed to changes in the hydration of the solutes, usually ions, at higher temperatures.

There have been many studies of the absorption spectra of salts in solution, the absorption of the solution being due in large part to absorption by the ions present. The influence of electrostatic forces upon the magnitudes of the extinction coefficients in various solutions and the effects of adding foreign non-absorbing salts have been investigated, but for present purposes it is sufficient to note that the effects of these electrostatic forces may be great enough to alter markedly the absorption region from that of the pure undissociated compound. The result may be that in solutions the photochemically effective wave-length regions may differ from those which induce the same reaction in the gas phase.¹¹ For example, the absorption band of the iodide ion found at 2273 Å in aqueous solution shifts toward shorter wave-lengths in concentrated calcium chloride solutions and in alcohol. Changes in the solvation of the ions are of importance in producing these effects.¹² Scheibe¹³ has reviewed the causes of variations in the absorption spectra of solutions.

Cations of the alkalis and alkaline earths do not absorb light, and visible or ultraviolet absorption exhibited by solutions of their salts is usually due to the anions. Other cations, as those of the transitional group of elements, iron, chromium, copper, cobalt, nickel, or manganese, exhibit absorption believed to arise from low-energy electron shifts involving the incomplete electron shell in the structure of these atoms.¹⁴

Electron-Affinity Spectra. The spectra of the anions, particularly those of the halogens, have been called "electron affinity spectra," since it is considered that the electron held by the atom or radical as ion is driven off from it in the absorption process, rather than excited to a higher energy state.¹⁵ The iodide ion exhibits two broad continuous bands with maxima at about 2250 and 1950 Å (see Figure 113). The separation between these maxima when expressed as the difference in the corresponding wave-numbers (about 8000 cm^{-1} .) is very close to the difference between the ground state and an excitation state of the iodine atom (7600 cm^{-1} .). Thus one maximum is interpreted as caused by separation of an electron from a normal iodine ion and the other to separation of an electron from an excited ion. The hydration of the ion and the hydration of the electron modify the results somewhat. Franck and Haber¹⁶ have postulated that, as a part of the process, the electron attaches itself to an OH group split off from a molecule of hydration of the ion, a hydrogen atom being also formed. Similar considerations also apply to the spectra of other anions, but in the more complex ones, as the nitrate ion, other decomposition possibilities must also be considered. Farkas and Farkas modify the theory by assuming that the primary process involves a

⁹ Hantzsch, A., and Carlsohn, H., *Z. anorg. Chem.*, **156**, 199 (1926).

¹⁰ Mukerji, B. K., Bhattacharji, A. K., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1834 (1928).

¹¹ von Halban, H., and Ebert, L., *Z. physik. Chem.*, **112**, 321 (1924); von Halban, H., *Trans. Faraday Soc.*, **21**, 620 (1926); von Halban, H., and Eisenbrand, J., *Z. physik. Chem.*, **122**, 337 (1926).

¹² Scheibe, G., with Römer, R., and Rössler, G., *Ber.*, **59B**, 1321, 2616 (1926).

¹³ Scheibe, G., *Angew. Chem.*, **50**, 212 (1937).

¹⁴ Saha, M., *Nature*, **125**, 130 (1930); Shibata, Y., and Harai, K., *J. Chem. Soc. Japan*, **56**, 1 (1935); Pestemer, M., and Bernstein, P., *Z. anorg. allgem. Chem.*, **223**, 121 (1935); Samuel, R., and others, *Z. physik. Chem.*, **22B**, 431 (1933); *Bull. Acad. Sci. United Provinces Agra Oudh, Allahabad*, **3**, 157 (1934); *Trans. Faraday Soc.*, **31**, 423 (1935); *Indian J. Physics*, **9**, 491 (1935); Inoue, T., *J. Chem. Soc. Japan*, **54**, 65 (1933); *Chem. Abs.*, **21**, 2382 (1933).

transfer of the electron from the anion to a water molecule in the hydration layers. If no photochemical change ensues, the electron returns to the initial state. If a reaction occurs, the final state is reached by the transfer of the electron to a positive ion. Thus,

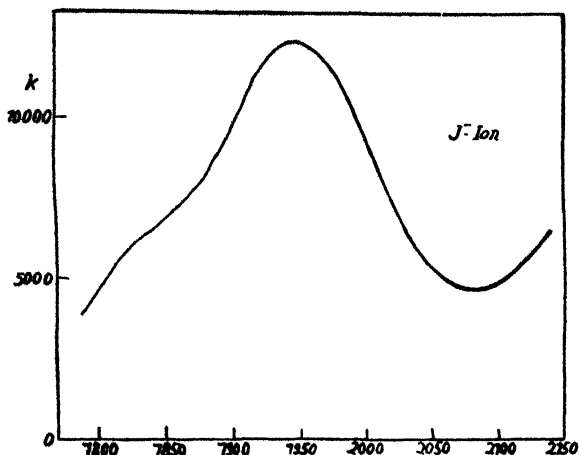
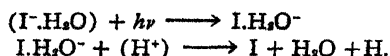


FIGURE 113. Electron Affinity Spectrum for Iodide Ion (Franck and Scheibe, *Z. physikalische Chemie*).

Lederle¹⁷ concludes, as a result of measurements of the electron-affinity spectra of aqueous and alcoholic solutions of alkali and alkaline earth halides, that the effects of temperature and solvent may be satisfactorily explained by the hypothesis of Franck and Scheibe. The hydroxyl ion has an absorption maximum at 1860Å.¹⁸

Since the theory of photochemical reactions in liquid systems is less advanced than is that of reactions in gaseous systems, the treatment of much of the material in this chapter is necessarily of a more descriptive and qualitative nature than that of the preceding chapter. On the other hand, photochemical processes in crystals, particularly the alkali and silver halides, are now being very actively studied from a theoretical standpoint.

WATER AND HYDROGEN PEROXIDE

Water is very transparent to ultraviolet wave-lengths greater than 1950Å, but below this its transparency decreases rapidly.¹⁹ Although earlier observers²⁰ had

¹⁵ Franck, J., and Scheibe, G., *Z. physik. Chem.*, **4B**, 22 (1928); **5B**, 355 (1929); Fromherz, H., and Menschick, W., *Z. physik. Chem.*, **7B**, 439 (1930); Farkas, A., and Farkas, L., *Trans Faraday Soc.*, **34**, 1113 (1938).

¹⁶ Franck, J., and Haber, F., *Ber. Berl. Akad.*, 250 (1931); Scheibe, G., *Z. Elektrochem.*, **35**, 701 (1929); *Sitzb. phys.-med. Soc. Erlangen*, 58-59 (1927); *Chem. Abs.*, **22**, 4371 (1928). See also Dutta, A. K., *Trans. Bose Research Inst., Calcutta*, **10**, 209 (1934-5), *Chem. Abs.*, **32**, 3263 (1938); Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1113, 1120 (1938).

¹⁷ Lederle, E., *Z. physik. Chem.*, **10B**, 121 (1930).

¹⁸ Ley, H., and Arends, B., *Z. physik. Chem.*, **6B**, 240 (1929).

¹⁹ Tsukamoto, K., *Rev. d'optique*, **7**, 89 (1928); for data throughout the visible see Hulburt, E. O., and Dawson, L. H., *J. Opt. Soc. Am.*, **24**, 175 (1934) and for sea water, Hulburt, E. O., *Ibid*, **17**, 15 (1928).

²⁰ Kernbaum, M., *Farm. Polsk.*, **16**, 71 (1913); *Chem. Abs.*, **8**, 387 (1914).

concluded that ultraviolet rays, and even the rays of the sun, would cause some decomposition of pure oxygen-free water, with the production of hydrogen peroxide, subsequent work has shown that only radiations of very short wave-length²¹ (1900A) produce any effect. Tian states that if the water contains dissolved oxygen, this may react with the hydrogen set free in the primary decomposition to form hydrogen peroxide. Ozone, formed from oxygen, may further react with hydrogen peroxide.²² Further work is needed.

It has been found by Bowden²³ that if, during the electrolysis of dilute sulfuric acid, the mercury cathode is irradiated by wave-lengths less than 4000A, there is a marked acceleration of the deposition of hydrogen. A similar effect occurs with respect to the liberation of oxygen at a platinum electrode, but the threshold wave-length was not determined.²⁴

The sensitized formation of hydrogen peroxide in the presence of aqueous suspensions of zinc oxide (in contact with air) when exposed to sunlight has been described by Baur and Neuweiler,²⁵ who represent the process in terms of the "molecular electrolysis" theory of photosensitization discussed in Chapter 16. The yield was said to be greatly increased in the presence of small amounts of glycerol, dextrose or benzidine, these added substances being simultaneously oxidized. When glycerol was employed, there was an indication of the formation of dihydroxyacetone and possibly glycerose; with benzidine, a brown, insoluble oxidation product resulted. When the sensitizer was eosin or fluorescein rather than zinc oxide, the formation of hydrogen peroxide could be observed only when dextrose or benzidine, but not glycerol, was present.

The Decomposition of Hydrogen Peroxide. In solutions, the coefficients of absorption of hydrogen peroxide are the same as those for the vapor.²⁶ The absorption, which begins between 3700 and 3800A, is but slight to 3000A, after which it increases rapidly with decreasing wave-length. In Figure 112, the circles represent values for the solutions and the crosses those for the vapor. Sharma²⁷ concludes the abrupt termination of the absorption spectra of 3, 10 and 30 per cent solutions at 2055A to correspond to the dissociation $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{H} + \text{O}_2$.²⁸ The progressive addition of alkali displaces the absorption curves toward longer wave-lengths, a limiting value of the shift (500A) being attained when the ratio of alkali to peroxide is one to one. The new absorption is attributed to the ion HO_2' , the formation of which involves a change in the mode of interatomic linking.²⁹

It was early found that the velocity of decomposition of hydrogen peroxide in dilute aqueous solution increases with increasing frequency of the radiation employed.³⁰ It has been observed that with dilute solutions of the peroxide, the velocity is dependent on the concentration.³¹ Tian and also Henri and Wurmser

²¹ Tian, A., *Compt. rend.*, **156**, 1063 (1913); Houben, J., and Fischer, W., *Arb. biol. Reichs. Land-Forstw.*, **15**, 601 (1928); *Chem. Abs.*, **23**, 2366 (1929); Coehn, A., *Ber.*, **43**, 880 (1910).

²² See also Kernbaum, M., *Compt. rend.*, **149**, 273 (1929).

²³ Bowden, F. P., *Trans. Faraday Soc.*, **27**, 505 (1931).

²⁴ See also Audubert, R., *Compt. rend.*, **189**, 1265 (1929).

²⁵ Baur, E., and Neuweiler, C., *Helv. Chim. Acta*, **10**, 901 (1927).

²⁶ Urey, H. C., Dawsey, M. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929).

²⁷ Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

²⁸ For a comparison with the absorption of mono- and di-alkyl peroxides, see Lederle, E., and Rieche, A., *Ber.*, **62B**, 2573 (1929).

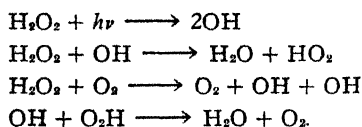
²⁹ Bredig, G., Lehmann, H. L., and Kuhn, W., *Z. anorg. Chem.*, **218**, 16 (1934).

³⁰ Tian, A., *J. Chem. Soc.*, **108** (ii), 828 (1915); *J. Soc. Chem. Ind.*, **35**, 114 (1916); *Chem. Abs.*, **10**, 1960 (1916).

³¹ Tian, A., *J. c.*; Kornfeld, G., *Z. wiss. Phot.*, **21**, 66 (1921); Henri, V., and Wurmser, R., *Compt. rend.*, **157**, 1261 (1913); **156**, 1012 (1913).

believed the velocity of decomposition to be proportional to the intensity of the incident radiation rather than to that absorbed. Qureshi and Rahman⁸² state however, that the rate is proportional to the square root of the light intensity. In recent observations, Kornfeld⁸³ concluded that in neutral solutions, the rate of decomposition produced by the 3110A line is proportional to the product of the concentration of hydrogen peroxide and the square root of the absorbed light. This relationship fails in acid solutions. This may have been a contributing factor in causing the divergent results of previous observers. Also Kornfeld noted that the quantum yield is variable and large, sometimes being as high as 80.

The presence of dust in the water used as solvent has been found to affect the results,⁸⁴ the rate of decomposition being roughly proportional to the dust content. Qureshi and Rahman found the quantum yield to vary with decreasing concentration between about seven and three, there being a maximum of eleven at a concentration of 0.09 M. Kornfeld proposed a chain mechanism for the reaction applicable in the presence of sodium sulfate and sulfuric acid:



In neutral solutions longer chains might account for the higher yields. Heidt,⁸⁵ using light of high intensity at 3130A, found the quantum yield to approach unity as the concentration of the hydrogen peroxide was decreased to low values. As is usually the case with chain reactions, the decomposition is readily inhibited by traces of various substances. Henri and Wurmser observed this stabilizing action on hydrogen peroxide as early as 1913. Anderson and Taylor⁸⁶ noted that although many inhibitors might function by absorbing the effective rays, some of the most effective inhibitors did not absorb the destructive wave-lengths. Furthermore, the inhibitors in general acted much more effectively when placed within the solution than when employed as external light filters. Subsequent work on the susceptibility of chain processes to inhibitors has given a new conception of the action of the latter as efficient breakers of chains. This topic is discussed in somewhat greater detail in connection with the oxidation of sulfites, but for a more general treatment, the reader is referred to texts on the theory of chain reactions.⁸⁷

Among the most efficient inhibitors for decomposition of hydrogen peroxide found by Anderson and Taylor were ethylamine, aniline, phenol and quinine salts. Strong to fairly strong inhibitors included methyl benzoate, benzamide and acetanilide. Moderate inhibitors were hydrocinnamic acid, ethyl cinnamate methyl oxalate, ethyl alcohol and benzyl alcohol. Weak inhibitors included ethyl benzoate, ethyl phenylacetate, acetone, acetophenone, benzophenone and benzene. Acetic acid, ethyl acetate and acetamide had little or no effect. In most cases the concentrations of inhibitor employed ranged from 0.0001 to 0.005 per cent. Anderson and Taylor⁸⁸ concluded that inorganic bases are excellent inhibitors, inor-

⁸² Qureshi, M., and Rahman, M. K., *J. Phys. Chem.*, **36**, 664 (1932).

⁸³ Kornfeld, G., *Z. physik. Chem.*, **29B**, 205 (1935).

⁸⁴ Rice, F. O., and Kilpatrick, M. L., *J. Phys. Chem.*, **31**, 1507 (1927).

⁸⁵ Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 2840 (1932).

⁸⁶ Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 650 (1923).

⁸⁷ Semenov, N., "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935.

⁸⁸ Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 1210 (1923); see also Mathews, J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 521 (1914).

ganic acids are good inhibitors, bromides and chlorides have a moderate inhibitory action and other inorganic salts such as nitrites, sulfates and perchlorates, have no action. They found also that one hydroxyl ion inhibits as much as 25 hydrogen ions and that inhibition has a zero temperature coefficient.

Recently, Dain and Shvartz³⁹ concluded that the photochemical decomposition is defined by the rate equation:

$$-d(\text{H}_2\text{O}_2)/dt = kI^{1/2}(\text{H}_2\text{O}_2)^{1/2}.$$

At 75° and under irradiation by a mercury vapor lamp, the rate of decomposition is reduced to one-half by the addition of 91×10^{-4} mole per liter of dimethyl ketone, of 20×10^{-4} of methyl ethyl ketone, or of 26×10^{-4} of diethyl ketone. The correction for the internal absorption of light by the ketone was never over 5 per cent. The ratios of the velocities of the inhibited and uninhibited reactions are linear functions of the ketone concentration. They believe the ketones decrease the initial number of chains, rather than break those already formed.

The well-known catalytic activity of lead peroxide and of platinum in the thermal decomposition of hydrogen peroxide is said to be increased by previously exposing the catalysts to ultraviolet light.⁴⁰ Irradiation during thermal decomposition increases the activity of graphite, charcoal and lead peroxide as catalysts, but may decrease that of platinum. It is suggested that electrons are transferred from hydrogen peroxide molecules adsorbed on inactive regions of the catalyst to those on active centers.

Sensitization of the decomposition of hydrogen peroxide to visible light has long been known. Kistiakowsky,⁴¹ who used as sensitizer a mixture of potassium ferro- and ferricyanides, found the decomposition to follow a monomolecular course and to continue after the irradiation had ceased. According to Weigert,⁴² potassium ferrocyanide which has been irradiated will cause a reaction when added to hydrogen peroxide in the dark. The same phenomenon has been found also in the case of sodium nitroprusside by Qureshi,⁴³ who believes the irradiation of this compound produces some colloidal Prussian blue which may serve as a catalyst for the dark reaction.

The quantum yield for the bromine-sensitized reaction has been found by Livingston and Schoeld⁴⁴ to be less than unity, but Griffith and McKeown⁴⁵ find the yield much greater than one in blue light. They also deny the existence of a "photo-stationary" state in this system.

Notwithstanding the fact that the decomposition of hydrogen peroxide is so sensitive to dust, inhibitors and sensitizers, the reaction has been employed in actinometry by Koepe.⁴⁶ However, Sostmann⁴⁷ found this method of measuring radiations unreliable.

³⁹ Dain, B. Y., and Shvartz, A. S., *Acta Physicochim. U.R.S.S.*, **3**, 291 (1935); *J. Phys. Chem. (U.S.S.R.)*, **7**, No. 2 (1936); *Chem. Abs.*, **30**, 2109 (1936).

⁴⁰ Pisarshevskii, L. V., Korabel'nik, R. K., and Rinskaja, E. S., *Bull. Acad. Sci. U.R.S.S.*, **7**, 931 (1934); *Brit. Chem. Abs. A*, **47** (1935); *Chem. Abs.*, **29**, 2433 (1935).

⁴¹ Kistiakowsky, G. B., *Z. physik. Chem.*, **35**, 431 (1901).

⁴² Weigert, F., *Ann. Physik*, **24**, 261 (1907).

⁴³ Qureshi, M., *J. Phys. Chem.*, **35**, 656 (1931).

⁴⁴ Livingston, R., and Schoeld, E. A., *J. Am. Chem. Soc.*, **58**, 1244 (1936).

⁴⁵ Griffith, R. O., and McKeown, A., *J. Am. Chem. Soc.*, **58**, 2556 (1936).

⁴⁶ Koepe, H., *Arch. Kinderheilk.*, **89**, 26 (1929-30).

⁴⁷ Sostmann, H., *Strahlentherapie*, **51**, 359 (1934); *Chem. Abs.*, **29**, 1012 (1935).

PHOTOCHEMISTRY OF THE HALOGENS AND ALKALI HALIDES

The decomposition of 0.08 to 1.16 molar solutions of hydrogen iodide in hexane by a spark follows Einstein's law.⁴⁸ At the higher concentration, the quantum yield was, as in the gas phase, two. At lower concentrations, it dropped to one because the hydrogen and iodine atoms liberated by absorption may recombine as a result of collisions with the solvent molecules which carry off the excess energy. But in aqueous solutions, the specific photochemical yield, that is, the number of molecules decomposed per gram calorie absorbed, decreased with the use of increasing wave-lengths. This is contrary to the Einstein law, since at longer wave-lengths a constant amount of energy is divided between a greater number of smaller quanta and should, therefore, bring more molecules into reaction. Furthermore, the yields decreased rapidly as the concentrations of the aqueous solutions were decreased. In highly concentrated aqueous solutions (7.5 normal) the shortest wave-length used (2070Å) gave an apparent quantum yield greater than two. To explain this it was suggested that an activated hydrogen iodide molecule might react with several consecutive normal molecules. Warburg believed also that the iodide ion forms no free iodine when irradiated, any production of iodine resulting from a decomposition of hydrogen iodide molecules. This explanation is not in line with the theory of complete dissociation of strong electrolytes. The anomalous effect of the wave-lengths was assumed due to the existence of hydrates of hydrogen iodide, since in hexane solutions the behavior was normal with respect to wave-length.

Subsequent to the development of the Franck and Haber theory of the primary process of absorption by halogen ions, $I^-(H_2O) + h\nu \rightarrow I + II + OH^-$ it became evident that the low yields in dilute solution may be explained as due to a combination of the hydrogen and iodine atoms which result from this process. The resulting hydrogen iodide then dissociates into hydrogen ions and iodide ions, the former combining with the hydroxyl ion formed in the primary process to yield water. In this way the original system present before the absorption of light is restored. In higher concentrations, the mechanism of the primary process, contrary to the assumption of Warburg, remains the same. In this case, however, there are present so many $I^-(H_2O)$ ions that the hydrogen atoms produced in the primary process may collide with the hydrated ions (rather than with iodine atoms) to produce a second iodine atom, an hydroxyl ion and a hydrogen molecule. The two iodine atoms may then combine to form a molecule of iodine. In this way, the quantum yields increase with the concentration to a value of about two as in the gas phase reaction.⁴⁹

Butkov⁵⁰ studied the effect of various wave-lengths upon half-normal solutions of caesium, potassium and sodium iodides, and also upon more dilute solutions of the latter salt ($N/50$). He found that spark lines longer than 2700Å failed to cause liberation of free iodine, this wave-length agreeing with the beginning of the absorption band of the iodide ion. Various shorter wave-length lines, notably the 2573Å line, were effective in liberating iodine. In accordance with the Franck-Haber mechanism, the solutions in which iodine was liberated became more alkaline. The quantum yields in these experiments were, however, lower than those of Warburg and Rump in stronger hydrogen iodide solutions. Butkov

⁴⁸ Warburg, E., and Rump, W., *Z. Physik*, **47**, 305 (1928).

⁴⁹ Compare Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1120 (1938). They were particularly concerned with the separation of hydrogen isotopes, when heavy water was in the solvent.

⁵⁰ Butkov, K., *Z. Physik*, **62**, 71 (1930).

placed the limit for the reaction in bromides, in which the yields of free bromine were lower, between 2265 and 2313 Å. He was unable to detect the liberation of chlorine from chlorides, the absorption of the chloride ion being located at wavelengths shorter than 1900 Å.⁵¹

Oxidation of Iodides. Earlier observations of the liberation of iodine from solutions of potassium iodide were in most cases complicated by photo-oxidations, since oxygen was rarely excluded from the solutions.⁵² The influence of oxygen upon the photochemistry of potassium iodide has been shown quantitatively by Krauss and Bruchhaus.⁵³ An oxygen-containing solution on irradiation gave 4.92 per cent decomposition, but a similar solution previously boiled to remove the air, gave only a 0.76 per cent separation of iodine.

In testing the ability of variously colored glass bottles to protect drugs from the action of light, Jermstad and Østby⁵⁴ employed a 2-per cent potassium iodide solution to which had been added 4 per cent of dilute sulfuric acid. This was exposed in the bottles to be tested for one-half hour to a quartz lamp or for one hour to sunlight. A maximum separation of 1.5 mg. of iodine after this time was considered permissible. Black, red and all-brown glasses were satisfactory, although the latter gave 1.10 mg. of iodine in ultraviolet light or 0.50 mg. in sunlight. It is difficult to understand which components of the solution can absorb the wave-lengths available in such experiments, unless it might be the tri-iodide ion. It has been stated that even in darkness, hydrogen ions can catalyze oxidation to some extent.

Stobbe and Steinberger⁵⁵ found irradiation of alkaline solutions of potassium iodide in quartz or Uviol vessels to sunlight or the quartz mercury arc to cause a diminution of the alkalinity, probably because of the absorption of carbon dioxide from the air. If the solutions were originally but slightly alkaline, irradiation produced free iodine and hypoiodide. If the alkalinity was somewhat greater, iodate appeared also. In strongly alkaline solutions, the iodate was the only product. In neutral solutions there was but little reaction, but the addition of increasing amounts of carbon dioxide increased the photolysis through a maximum. The oxidation of neutral iodide solutions is a bimolecular reaction. The velocity coefficient is dependent on the wave-length and intensity of the light absorbed. It increases with time until so much tri-iodide ion has formed that the absorption of all available radiation is complete.

According to Berthoud and Nicolet,⁵⁶ the oxidation of hydriodic acid by oxygen in red light has a velocity which can be expressed by

$$\frac{d[I_2]}{dt} = k(KI)^2(O_2)\sqrt{I_0(I_2)}(\overline{H_2SO_4})$$

⁵¹ Extensive data on the absorption of liquid hydrogen chloride and concentrated hydrochloric acid solutions have been given by Tréhin, R., *Compt. rend.*, **191**, 774 (1930); **193**, 1089 (1931); **195**, 1269 (1932), **199**, 1047 (1934); **200**, 1663 (1935); *J. Phys. Radium*, **4**, 449 (1933). Data for a number of chlorides are included and indicate that in concentrated solutions these are not as transparent to the region 2170 to 2500 Å as had been assumed from measurements on more dilute solutions. See also Hutting, G., and Kukenthal, H., *Z. Elektrochem.*, **34**, 14 (1928) and Hantzsch, A., *Ber.*, **59B**, 1096 (1926). For earlier data, Getman, F. H., *J. Phys. Chem.*, **29**, 853 (1925), and Brannigan, P. J., and Macbeth, A. K., *Chem. Abs.*, **11**, 313 (1917). In the presence of free halogen, the absorption is altered because of the formation of trihalogen ions. Similar behavior is also encountered in alcoholic solutions, according to Job, P., *Compt. rend.*, **182**, 632, 1631 (1926).

⁵² Suryanarayana, K., *J. Sci. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924); *Chem. Abs.*, **18**, 3548 (1924); Ross, W., *J. Am. Chem. Soc.*, **28**, 788 (1906); Kailan, A., *Monatsh.*, **34**, 1225 (1913); *Chem. Abs.*, **8**, 14 (1914).

⁵³ Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930); *Brit. Chem. Abs.*, **A**, 553 (1930); earlier experiments were due to Plotnikow, J., *Z. physik. Chem.*, **58**, 214 (1907).

⁵⁴ Jermstad, A., and Østby, O., *Arch. Pharm. Chem.*, **92**, 463 (1935); *Chem. Abs.*, **29**, 7599 (1935).

⁵⁵ Stobbe, H., and Steinberger, F. K., *Z. anorg. Chem.*, **161**, 21 (1927).

In blue light, the velocity also increases as the square root of the light intensity. The photochemical reaction has a very small temperature coefficient, which Vita⁵⁷ believes depends in some manner upon the wave-length.⁵⁸ The influence of the presence of potassium dichromate and eosin in causing the separation of iodine from potassium iodide when illuminated has been studied by Reychler.⁵⁹

The conductance of solutions of sodium iodide or of lithium bromide in acetophenone, but not of the solvent itself, decreases to a constant value when the solutions are exposed to light, and is restored to its former value when the solutions are returned to darkness.⁶⁰ A yellow color also appeared during irradiation. These results were confirmed by Morgan, Lammert and Crist,⁶¹ who found also that solutions which had reached a constant conductance in glass would show a further decrease when placed in quartz vessels. The acetophenone is also decomposed with the formation of some benzoic acid. The quantity of iodine liberated from sodium iodide under these conditions was independent of the concentration of the salt, but depended upon the intensity of the radiation and the time of exposure, that is, upon the amount of acetophenone which had been decomposed.

The oxidation of ferrous ions by iodine, $2\text{Fe}^{++} + \text{I}_2 \rightarrow 2\text{Fe}^{+++} + 2\text{I}^-$, was found to be photosensitive⁶² in both the ultraviolet and the visible region of 5500 to 6500Å (maximum at 5800Å). Iodine, being present as the tri-iodide ion, was the photosensitive component of the solution, the iron salts or the iodide ion being practically inactive in the spectral regions employed. The temperature coefficient of the reaction is 1.17. From that of the dark reaction (2.71), it appeared that the energy of activation, 2.14 volts, was very close to a resonance potential of the iodine molecule (2.34 v.). For the wave-length 5790Å, the quantum yield was found to be unity, one molecule of iodine reacting per absorbed quantum. Kistiakowsky⁶³ found this quantum yield given also by the wave-lengths 5460Å, 4360 and 3660Å, regions which Rideal and Williams had found ineffective. This absence of a maximum sensitivity at 5800Å lessens the significance of the relation between the energy of activation and a critical potential of iodine noted by Rideal and Williams. By working with very dilute solutions at 0°C., and using light of wave-lengths greater than 5000Å which had been freed from infrared rays, Ravitz and Dickinson⁶⁴ were able to show that, in the first stages of irradiation, light caused a reduction of the ferric ion by the iodide ion.

Mukerji and Dhar⁶⁵ found the reactions between iodine and such compounds as potassium formate, oxalate, ferrous sulfate and sodium nitrite to be accelerated principally by light in the range 3160 to 4600Å. The quantum yields, calculated for 3880Å, were low in the case of potassium oxalate, ferrous sulfate and sodium nitrite since for the transformation of each molecule of iodine there were required

⁵⁶ Berthoud, A., and Nicolet, G., *Helv. Chim. Acta*, **10**, 475 (1927); van Strachow, N., *Z. wiss. Phot.*, **18**, 267 (1919); *Chem. Centrbl.*, **90** (III), 309 (1919).

⁵⁷ Vita, N., *Gazz. Chim. Ital.*, **63**, 211 (1933).

⁵⁸ For comparisons of the kinetics of the photooxidation of the iodides of hydrogen and deuterium, see Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935).

⁵⁹ Reychler, A., *Bull. Soc. Chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 545 (1926). See also Winther, C., *Z. physik. Chem.*, **A174**, 41 (1935) and Tappeiner, H., *Chem. Centr.*, **1**, 1793 (1906); *Arch. klin. Med.*, **86**, 478.

⁶⁰ Dutoit, Z., *Elektrochem.*, **12**, 642 (1906); Nicollier, *Thesis*, Lausanne, 1907.

⁶¹ Morgan, J. L. R., Lammert, O. M., and Crist, R. H., *J. Am. Chem. Soc.*, **46**, 1170 (1924).

⁶² Rideal, E. K., and Williams, E. G., *J. Chem. Soc.*, **127**, 258 (1925); for previous observations, Sasaki, N., *Z. anorg. Chem.*, **122**, 61 (1922).

⁶³ Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 976 (1927).

⁶⁴ Ravitz, S. F., and Dickinson, R. G., *J. Am. Chem. Soc.*, **53**, 3381 (1931).

⁶⁵ Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 621 (1925); Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931).

28, 15 and 49 quanta, respectively. In later work, Bhattacharya and Dhar⁶⁶ stated that the quantum yield in the reaction with sodium nitrite varies greatly at different temperatures and with different wave-lengths. The dark reaction is bimolecular and has a temperature coefficient of 2.7, that of the light reaction varying from 2.07 at 4725Å to 2.35 at 8500Å.

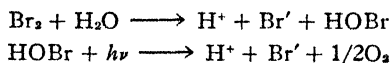
According to Batley,⁶⁷ the maxima observed in the absorption of alcoholic solutions of iodine at 3600 and 2900Å are due to the formation of HI_3 . When isolated in the solid form on gelatin, this has a maximum at 3680Å. The true iodine curve, determined in the presence of ozone which decomposed the hydrogen iodides, shows only one maximum at 4770Å and general absorption in the far ultra-violet. Formation of the hydrogen iodides is attributed to a slow photochemical reaction $C_2H_5OH + I_2 \rightarrow CH_3CHO + 2HI$, followed by an instantaneous reaction $I_2 + HI \rightarrow HI_3$.

Terenin⁶⁸ has studied the photochemical changes which occur in a layer of iodine molecules adsorbed on thallium iodide. Light, particularly of wave-length 5600Å, produces a discoloration attributed to photodissociation of adsorbed molecules. The liberated iodine atoms are then bound by thallium ions. The presence of adsorbed hydrogen or oxygen molecules on the surface causes marked shifts of the wave-lengths which are active, but nitrogen has no effect. The results are ascribed to photochemical reactions between adsorbed iodine and hydrogen or oxygen, with the formation of hydrogen iodide and of iodine oxide.

Potassium iodate, when irradiated by short wave-lengths in a solution saturated with carbon dioxide, liberates iodine at a rate which is linear so long as the amount liberated is small compared with the total amount present as iodate.⁶⁹ In the presence of air, the rate of the reaction decreases slowly with time. When the solution is kept saturated with oxygen, iodine is not liberated. Carbon dioxide greatly increases the rate of photolysis.

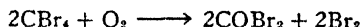
Bromine. Bovis⁷⁰ finds bromine in water, carbon tetrachloride, chloroform or alcohol to show two absorption maxima of which one lies at 4100Å and the other at 2600Å. Since only the former is also exhibited by gaseous and by liquid bromine, the band at 2600Å must be characteristic of bromine in solution.

Photochemical reaction between bromine and water appears to follow the reactions: ⁷¹



The rate decreases with increasing bromide-ion concentration.

In light of wave-length 4360Å, carbon tetrabromide is oxidized when present in concentrations above 0.05 mole per liter.



At lower concentrations, the oxygen consumption is greater. The quantum yield is less than one. The reaction is accelerated by oxygen, retarded by bromine and

⁶⁶ Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 709 (1930); *Chem. Abs.*, **25**, 251 (1931).

⁶⁷ Batley, A., *Trans. Faraday Soc.*, **24**, 438 (1928); cf. also Rabinowitsch, E., and Wood, W. C., *Ibid.*, **32**, 547 (1936).

⁶⁸ Terenin, A., *Acta Physicochim. U.R.S.S.*, **1**, 178, 407 (1934); *Chem. Abs.*, **29**, 685, 7810 (1935). *Brit. Chem. Abs.*, **A**, 943 (1935).

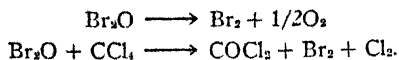
⁶⁹ Mathews, J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 641 (1914); *J. Chem. Soc.*, **106** (ii), 830 (1914).

⁷⁰ Bovis, P., *Compt. rend.*, **185**, 57 (1927).

⁷¹ Pagel, H. A., and Carlson, W. W., *J. Phys. Chem.*, **40**, 613 (1936).

unaffected by bromophosgene.⁷² The suggested mechanism involves the primary removal of a bromine atom, which requires at most 50 kcal. The resulting CBr_3 then reacts with the oxygen.

Bromine oxide, Br_2O , prepared by the interaction of mercury oxide and bromine in carbon tetrachloride solution, decomposes in light by the following two reactions:⁷³



The maximum rate of decomposition of bromine chloride in the light is four times that in the dark. The quantum yield is of the order of a thousand.⁷⁴

Chlorine. That sunlight decomposes chlorine water with the formation of oxygen and chlorides, or under certain circumstances, of chlorites and chlorates, has long been known. The loss of active chlorine in bleaching solutions in daylight has been found to be after 70 days in filled white glass bottles, 48 to 61 per cent, in half-filled bottles, 63 to 76 per cent and in half-filled brown bottles, 11 to 29 per cent.⁷⁵

Free hypochlorous acid is said to be less sensitive to light than the sodium salt.⁷⁶ Sunlight, diffused daylight and the lines at 3130, 3650 and 4360A, appeared equally effective.⁷⁷ Despite repeated and detailed investigations, the interpretation of the reaction is not yet entirely clear. Neither hydrogen peroxide nor perchloric acid is formed, the only reaction products being hydrochloric acid, oxygen and chloric acid. To determine whether chlorine, hypochlorous acid or its ion is the photosensitive substance, Allmand and co-workers studied the effects on the rate and products formed, of the addition of various salts which might shift the equilibrium in the irradiated solutions. From the retarding effects of chlorides⁷⁸ or hydrochloric acid and the accelerating effects of buffer salts, they concluded that hypochlorous acid plays a more important part in the primary process than chlorine. The latter could not, however, be excluded, so that it was necessary to conclude that there may be two independent primary processes and two reaction mechanisms. In one at least, atomic oxygen was regarded as a primary product which, reacting with hypochlorous acid, produced chloric acid. When chlorine water was irradiated with a filtered band of mean wave-length 3650A, the quantum yield was approximately two. This was greatly decreased by the addition of hydrochloric acid (to 0.054 in 0.6N HCl). They believed an analysis of their data permitted an estimation of the quantum yield of the primary process (as distinguished from that of the overall reaction) as approximately unity. The temperature coefficient of the overall reaction was given as 1.4 by Benrath and Tüchel.⁷⁹

The decomposition of sodium hypochlorite in neutral or alkaline solutions by wave-lengths in the range 4360-2130A was found to follow a monomolecular course

⁷² Koblitz, W., Meissner, H., and Schumacher, H. J. *Ber.*, **70B**, 1080 (1937)

⁷³ Brenschede, W., and Schumacher, H. J. *Z. physik. Chem.*, **29B**, 356 (1935).

⁷⁴ Brauer, G., and Victor, E., *Z. Elektrochem.*, **41**, 508 (1935)

⁷⁵ Tuenter, J. P. A., *Chem. Weekblad*, **32**, 429 (1935); *Chem. Abs.*, **30**, 28 (1936); see also, Fowler, J. *Chem. Soc.*, **94**, (II), 914 (1908); Kling, A., and Schmutz, R., *Compt. rend.*, **192**, 1655 (1931) and Jacquemaine, R. P., and Doll, J. H., *Bull. Soc. Chim.*, **2**, 1669 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935).

⁷⁶ Bonnet, L., *Rev. gen. mat. color.*, **39**, 29 (1935); *Chem. Abs.*, **29**, 2312 (1935).

⁷⁷ Allmand, A. J., Cunliffe, P. W., and Maddison, R. E. W., *J. Chem. Soc.*, **127**, 655, 822 (1925).

⁷⁸ See, however, Shilov, E. A., and Kupinskaya, G. V., *Byull. IvNITI*, **12**, No. 6, 39 (1936); *Chem. Abs.*, **31**, 3288 (1937).

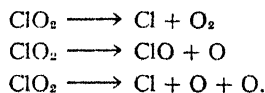
⁷⁹ Benrath, A., and Tüchel, H., *Z. wiss. Phot.*, **13**, 383 (1913).

by Lewis.⁸⁰ Allmand and Webb⁸¹ found the proportion of sodium chlorate formed (40 to 53 per cent) to be independent of the intensity of illumination, hypochlorite concentration (0.08 to 0.01 molar) and of the concentrations of chloride, sulfate and free alkali. At higher dilutions, the yield of chlorate diminished. However, the yield of the latter increased with frequency of the light. The quantum yield was about unity at 3650A, slightly higher, 1.2, at 3130A and much higher, 4.7, at 2540A. The addition of electrolytes had an effect opposite to that previously noted in the case of hypochlorous acid or chlorine water. Thus, sodium chloride increased the quantum yield.

Chlorine Monoxide. Bowen stated that light (4100-4700A) acting on chlorine monoxide in carbon tetrachloride solution⁸² caused formation of chlorine and oxygen. The quantum efficiency was calculated to be 0.81 to 1.02, on the assumption that these were the only products formed. In later work, however, Bowen observed that in the gaseous state two molecules of chlorine monoxide were decomposed by each absorbed quantum.⁸³ In the decomposition of chlorine monoxide in solution chlorine dioxide appears in appreciable amounts in comparison with the amount of monoxide decomposed, according to Dickinson and Jeffreys.⁸⁴ Using a method devised to eliminate the effects of the chlorine dioxide formed, they found that in solutions 0.014 to 0.054 molal in chlorine monoxide, the initial yield of chlorine dioxide is about 0.35 molecule per quantum absorbed. The initial rate of the decomposition of the chlorine monoxide has a quantum yield of at least 1.8. In a given run, the amount of the dioxide formed increases less and less rapidly with the number of quanta absorbed as the exposure is prolonged. This is possibly because the dioxide acts itself as an internal filter and also because it is also subject to photochemical decomposition.

Chlorine Dioxide. The decomposition of chlorine dioxide in carbon tetrachloride solutions (0.0346 to 0.317 molar) by blue and violet light was believed by Bowen⁸⁵ to have a quantum efficiency of unity. A repetition of this work by methods⁸⁶ which also took into account the rapid dark reaction,⁸⁷ changed this value to two when the 4150A line was employed. The initial concentrations were 10.4 to 33.3 millimoles of chlorine dioxide per liter. Filters were used to limit the light to 4100 to 4200A. The filters were 30 mm. of a solution of 5.5 per cent of cobaltous sulfate (7 H₂O) and 8 per cent of ammonium thiocyanate and 30 mm. of a solution containing 25 per cent of copper sulfate (5 H₂O) and 0.04 per cent of quinine sulfate.

Since this radiation falls in the banded region of the spectrum of gaseous chlorine dioxide, it was assumed that activated molecules are formed. These on collision with the solvent molecules suffer decomposition by one of the following schemes:



⁸⁰ Lewis, W. C. McC., *J. Chem. Soc.*, **101**, 2371 (1912); Spencer, L., *Ibid.*, **105**, 2565 (1914).

⁸¹ Allmand, A. J., and Webb, W. W., *Z. physik. Chem.*, **131**, 189 (1928).

⁸² Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

⁸³ Bowen, E. J., *J. Chem. Soc.*, **123**, 2330 (1923).

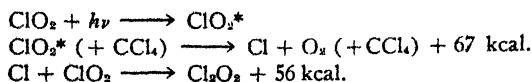
⁸⁴ Dickinson, R. G., and Jeffreys, C. E. P., *J. Am. Chem. Soc.*, **52**, 4288 (1930). It had, indeed, been observed to form in the gas phase reaction by Kistiakowsky, G. B., and Bodenstein, M., [*Z. physik. Chem.*, **116**, 371 (1925)], who believed the amounts small enough not to interfere with quantum yield measurements.

⁸⁵ Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

⁸⁶ Nagai, Y., and Goodeve, C. F., *Trans. Faraday Soc.*, **27**, 508 (1931).

⁸⁷ Luther, R., and Hoffmann, R., *Z. physik. Chem. Bodenstein-Festband*, 755 (1931).

It was believed that both of the two latter modes of decomposition required greater amounts of energy (80-85 kcal. for the second and 119 kcal. for the third) than is available at 4150A (69 kcal.). The first reaction is endothermic to the extent of only 2 kcal. For this reason the proposed mechanism which accounts for the yield of two, is



Bowen and Cheung⁸⁸ found the quantum yield to increase from one at 4360A to two at 4050A or shorter wave-lengths. In aqueous solutions, the rate of photodecomposition was found proportional to the light intensity and the quantum yields were lower, being 0.2 at 4360A and unity at 3000A. Chlorine, chloride ion, and chlorate ions were identified. It was suggested that in solution, chlorine dioxide undergoes predissociation at lower energy values than it does as a gas.

In stable solutions prepared by washing the chlorine dioxide solutions with weakly alkaline materials, Luther and Hoffmann⁸⁹ found, after a pre-exposure to light, a decomposition to occur in the dark at a rate proportional to the four-thirds power of the concentration of chlorine dioxide. They suggested that chlorine monoxide liberated during the exposure to light may have induced the dark reaction. They also observed that the photolysis in ultraviolet light is a reaction of zero order. Spinks and Taube⁹⁰ find relatively large amounts of chlorine hexoxide, chlorine heptoxide and chlorine monoxide to be formed in addition to chlorine and oxygen. For a bromine-sensitized decomposition by the line 5460A, the quantum yield is 0.2 to 0.3.

Chlorates. Oertel⁹¹ found that under the action of ultraviolet rays the alkali salts of chlorates, bromates, iodates and periodates in aqueous solution decompose into oxygen and halogen quantitatively if the exposure is sufficiently prolonged. Only a very small decomposition could be observed in the case of perchlorates. The rate of decomposition of bromates was greater than that of iodates and that of iodates greater than that of chlorates. Suryanarayana⁹² states that neutral potassium chlorate and potassium nitrate solutions liberate oxygen on exposure to ultraviolet, but that equilibrium is quickly established. Exposure of a mixture of potassium chlorate and iodide with exclusion of oxygen leads to the oxidation of the iodide.

Solid potassium chlorate evolves oxygen when irradiated by radiations of wave-lengths shorter than about 2800A.⁹³ The decomposition may also be brought about by the impact of 22-volt electrons, but those of lower voltages corresponding with 2800A could not be shown to be effective. According to Krishnan and Narayanaswamy,⁹⁴ photodissociation of the crystals shows an anisotropic effect, linearly polarized light producing a greater effect when the electric vector is in the plane of the chlorate ion than when it is along the normal to this plane.

⁸⁸ Bowen, E. J., and Cheung, W. M., *J. Chem. Soc.*, 1200 (1932).

⁸⁹ Luther, R., and Hoffmann, R., *Z. physik. Chem.*, 117A, 17 (1936).

⁹⁰ Spinks, J. W. T., and Taube, H., *J. Am. Chem. Soc.*, 59, 1155 (1937); *Can. J. Research*, 15B, 499 (1937); *Chem. Abs.*, 32, 2028 (1938).

⁹¹ Oertel, W., *Biochem. Z.*, 60, 480 (1914); *J. Chem. Soc.*, 106 (11), 321 (1914).

⁹² Suryanarayana, K., *J. Assoc. Maharajah's College, Visianagaram*, 2, 12 (1924); *Chem. Abs.*, 18, 3548 (1924).

⁹³ Meiler, J. G., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, 52, 527 (1930).

⁹⁴ Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, 3, 417 (1935); *Brit. Chem. Abs.*, A, 682 (1935).

Mack⁹⁵ has stated that chlorates may be electrolytically oxidized to perchlorate in an acid solution in the presence of oxygen activated by ultraviolet rays.

Fluorine Oxide. This compound absorbs ultraviolet light, but according to v. Wartenberg and Klinkott⁹⁶ is not decomposed by it. Palmer⁹⁷ finds that light from a hydrogen discharge tube on passing through a fluorite window into air at atmospheric pressure, caused the formation of a film on the outside of the window and upon this film a white powder. The film with metallic luster is soluble in alcohol and is probably calcium oxyfluoride. The powder, which forms more rapidly in moist air, is insoluble in water, but soluble in dilute hydrochloric acid.

COMPOUNDS OF NITROGEN

Ammonia. Pure liquid ammonia begins to absorb at about 2500A, the absorption increasing rapidly and being complete at about 2350A. The absorption also increases as the temperature rises, the threshold for absorption changing from 2320A at -78° to 2580A at 26°C . In aqueous solutions absorption increases with concentration, but is always less than that of the same number of ammonia molecules in the liquid or gaseous state.⁹⁸

No reaction occurs when pure liquid ammonia is exposed to the wave-length 2300A, although this radiation is capable of causing the decomposition of gaseous ammonia.⁹⁹ Similarly, in water solution, the yield is kept low by recombination in triple collisions of the dissociation products H and NH_2 with the solvent molecules.

Kuhn¹⁰⁰ states that when ultraviolet rays of wave-lengths 2025 to 2140A fall on the compound $2\text{AgCl} \cdot 3\text{NH}_3$, the ammonia is decomposed.

The irradiation of solutions of alkali metals in liquid ammonia causes a reaction producing the amide ion and hydrogen.¹⁰¹ The quantum efficiency is a function of both the metal concentration and the wave-length. There is a definite long wave-length threshold at about 2600A and a maximum quantum efficiency at about 2300A. The absorption is similar to that of liquid ammonia. In solutions of the alkali metals, the metal is almost completely dissociated into positive ions and solvated electrons. If the electron collides with the amide radical (produced by photodissociation) before the latter recombines with the hydrogen atom, an amide ion results and the hydrogen then has a greater opportunity to combine with another hydrogen atom. Since the probability that an amide radical will collide with electrons increases with the concentration of the latter, the quantum efficiency should be expected to increase regularly with the concentration, starting at zero and approaching unity asymptotically. This was found to be the case. Since the positive ion plays no essential part in the process, the quantum efficiency should be independent of the nature of the metal. This was true except for deviations encountered with caesium.

The amides of sodium and potassium show very strong continuous absorption throughout the ultraviolet with a maximum near the long wave-length thresholds of 3800-3900A for sodium, and 3950-4150A for potassium, amide. The absorption of light by the electron-ammonia complex, being photochemically inactive, lowers

⁹⁵ Mack, E. L., *J. Phys. Chem.*, **21**, 238 (1917).

⁹⁶ v. Wartenberg, H., and Klinkott, G., *Z. anorg. allgem. Chem.*, **193**, 409 (1930). See also Glissman, A., and Schumacher, H. J., *Z. physik. Chem.*, **B24**, 328 (1934).

⁹⁷ Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).

⁹⁸ Briot, A., and Vodar, B., *Compt. rend.*, **201**, 500 (1935).

⁹⁹ Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).

¹⁰⁰ Kuhn, W., *Compt. rend.*, **177**, 956 (1923); *Chem. Abs.*, **18**, 789 (1924); *J. chim. Phys.*, **23**, 521 (1926).

¹⁰¹ Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).

the quantum efficiency and accounts for the final yield being less than unity. This work gave a direct method of detecting the NH_2 radical as one of the products of the photodissociation of ammonia. From thermal considerations and the absorption of the metal amides, it appeared that sodium amide is optically dissociated into a normal state sodium atom and a normal state amide radical and is, therefore, ionically bound.

Fearon and M'Kenna¹⁰² state that urea is produced by exposing ammonium carbonate to rays of wave-lengths 2000 to 2500 Å. The yield is thought to be increased in the presence of malachite green.

In the presence of oxygen or air, solutions of ammonia are oxidized to nitrites when exposed at 35° to 50°C. for three to nine hours to the radiations of a mercury arc.¹⁰³ Nitrates were not formed. Ammonium salts were also oxidized to nitrites, the reaction being slower in the case of the sulfate and chloride than in that of the carbonate. Corbet¹⁰⁴ finds hyponitrous acid to be formed as an intermediary product. Gion¹⁰⁵ claimed to have observed the formation of some nitrate in ammonia solutions exposed in quartz vessels to the radiations of a mercury arc. The oxidation proceeded faster at lower temperatures. He claimed also that if only the oxygen in contact with the ammonia solutions and not the solution itself, were irradiated there was oxidation by the ozone formed in the gas. The reaction was said to be sensitized by zinc or titanium oxides.

According to Baur and Renz,¹⁰⁶ ammonia is oxidized to nitrate, and oxalic acid to carbon dioxide on illumination when these substances are adsorbed on thallos chloride. The latter is itself converted to the photochloride.

The acceleration of the photochemical oxidation of ammonia by natural or artificial humus substances¹⁰⁷ or by various catalysts, such as titanium dioxide, alumina or zinc oxide present in soil, has been the subject of many observations, particularly by Indian chemists.¹⁰⁸ Most of these workers believe that ammonium salts are converted through nitrites to nitrates by sunlight in soils under the influence of sensitizers, but some also believe that various organic nitrogen compounds, including urea, amino-acids and uric acid, may similarly yield nitrites and nitrates.

Other workers tend to minimize the importance of photochemical processes in the soil. Fraps and Sterges¹⁰⁹ found that in a large group of samples with different ammonium salts, on the average 5 per cent of the ammonia was oxidized in the sunlight and 41 per cent in the dark. In all cases with corresponding bacterial cultures, those in the dark were oxidized more completely than those in the light. In sterile soils there was no evidence of nitrification. Nitrites in small amounts were found in cultures exposed to light, but little or none in those kept in

¹⁰² Fearon, W. R., and M'Kenna, C. B., *Biochem. J.*, **21**, 1087 (1927).

¹⁰³ Kuhn, W., *Compt. rend.*, **152**, 522 (1911).

¹⁰⁴ Corbet, A. S., *Biochem. J.*, **28**, 1575 (1934); **29**, 1086 (1935); Gion, L., *Compt. rend.*, **196**, 344 (1933).

¹⁰⁵ Gion, L., *Compt. rend.*, **195**, 421 (1932).

¹⁰⁶ Baur, E., and Renz, C., *Helv. Chim. Acta*, **15**, 1085 (1932).

¹⁰⁷ Zolcinski, J., *Rocz. Nauk Rolniczych*, **10**, 311 (1923); *Chem. Zentr.*, **96**, I 1123 (1925)

¹⁰⁸ Dhar, N. R., Bhattacharya, A. K., and Biswas, N. N., *Soil Sci.*, **35**, 281 (1933); Rao, G. G., *Soil Sci.*, **38**, 143 (1934); Dhar, N. R., and Tandon, S. P., *J. Indian Chem. Soc.*, **13**, 180 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936); Sarkaria, A. R., and Fazal-Ud-Din, *Indian J. Agr. Sci.*, **3**, 1057 (1933); **5**, 195 (1935); Desai, S. V., and Fazal-Ud-Din, *Ibid.*, **6**, 777, 985 (1936); Dhar, N. R., and Mukerji, S. K., *J. Indian Chem. Soc.*, **12**, 756 (1936); **13**, 23, 535 (1936); Dhar, N. R., Tandon, S. P., and Mukerji, S. K., *Ibid.*, **12**, 67 (1935); Osugi, S., and Aoki, M., *J. Sci. Soil Manure (Japan)*, **10**, 11 (1936); *Chem. Abs.*, **30**, 3029 (1936). Dhar has summarized his work on the influence of light on nitrogen fixation in soils in *Proc. Natl. Acad. Sci. India*, **6**, Business matters, 3, 289 (1936); *Chem. Abs.*, **31**, 6392, 6393 (1937); see also Dhar, N. R., Mukerji, S. K., Seshacharyulu, E. V., and Tandon, S. P., *Proc. Natl. Inst. Sci. India*, **3**, 75 (1937); *Chem. Abs.*, **32**, 1840 (1938).

¹⁰⁹ Fraps, G. S., and Sterges, A. J., *Soil Science*, **39**, 85 (1935); *Chem. Abs.*, **29**, 4867 (1935).

darkness. This was taken to indicate that the nitric organisms are less resistant to light than are the nitrous organisms. A few non-sterile cultures of soil treated with ammonium salts and exposed to sunlight contained slightly more nitrate and nitrite than did the corresponding soils kept in darkness. These small increases were, however, attributed to differences in bacterial activity rather than to photonitrification. These authors did not regard their work as eliminating the possibility of photonitrification, but thought that photonitrification has a relatively slight effect upon soil processes.¹¹⁰

Nitrites. Sodium nitrite absorbs between 3000 and 4000 Å.¹¹¹ In 2-per cent aqueous solution in a glass cell, the nitrite almost completely absorbs the 3660 Å line. Although Berthelot and Gaudechon¹¹² had claimed nitrogen to be evolved as a result of the insolation of ammonium nitrite, Holmes¹¹³ was unable to detect any loss of nitrite from a 2.5*N* solution of ammonium nitrite exposed in a quartz vessel for six hours to a 110-volt quartz mercury arc at a distance of 8-16 cm.

Nitrous acid can, however, be decomposed. Mukerji and Dhar¹¹⁴ found the velocity coefficients in both the light and dark reactions



to increase slowly with increasing concentrations of nitrous acid. The velocity was markedly accelerated by light, especially when closed vessels were used. Also, the velocity is proportional to the cube root of the light intensity, according to Murty and Dhar,¹¹⁵ who employed the wave-lengths 4725, 5650, 7304 and 8500 Å. The temperature coefficient is less than unity and the Einstein law does not apply.

The influence of light upon the reaction between iodine and potassium nitrite has been studied by Berthoud and Berger.¹¹⁶ The overall reaction is $\text{KNO}_2 + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{KNO}_3 + 2\text{HI}$. In blue light the temperature coefficient is 1.30 between 35° and 45°C. The quantum yield is low, 22 quanta being required to cause one molecule of iodine to react in a solution containing 0.1 mole of potassium iodide and 1 mole of nitrite.¹¹⁷ In the case of sodium nitrite, the quantum yield varies from 0.005 to 0.1 in phosphate buffers. The yield is independent of the pH, initial concentration of iodine, and rate of absorption of energy (4360 Å, 5460 Å, 5790 Å), but depends on the wave-length, temperature and concentrations of nitrite and iodine atoms. Also, the quantum yield decreases with increasing ionic strength.¹¹⁸

Nitrates. The absorption of light by the nitrate ion has been much studied.¹¹⁹ It consists of two broad bands with maxima at 3100 and at about

¹¹⁰ See also Corbet, A. S., *Trans. Third Intern. Congress Soil Sci., Oxford*, **1**, 133 (1935); Waksman, S. A., Madhok, M. R., and Hollaender, A., *Soil Sci.*, **44**, 441 (1937); *Chem. Abs.*, **32**, 1376, 2670 (1938); Nath, B. V., *Sci. Repts. Imp. Agr. Research Inst. New Delhi*, **98** (1937); *Chem. Abs.*, **32**, 4265 (1938); Joshi, N. V., and Biswas, S. C., *Trans. Third Intern. Congr. Soil Sci., Oxford*, **3**, 104 (1935); *Chem. Abs.*, **32**, 5567 (1938).

¹¹¹ Weber, K., *Chem. Ztg.*, **56**, 642 (1932); *Phot. Korr.*, **66**, 317 (1930).

¹¹² Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

¹¹³ Holmes, M., *J. Chem. Soc.*, 1898 (1926).

¹¹⁴ Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 255 (1925).

¹¹⁵ Murty, K. S., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 985 (1930); *Chem. Abs.*, **25**, 2921 (1931).

¹¹⁶ Berthoud, A., and Berger, W. E., *Helv. Chim. Acta*, **11**, 354 (1928); *J. chim. phys.*, **25**, 542 (1928).

¹¹⁷ It was pointed out that previous work by Mukerji, B., and Dhar, N., [*Z. Elektrochem.*, **31**, 621 (1925)] was in error because of the use of an unsuitable analytical method.

¹¹⁸ Durrant, G. G., Griffith, R. O., and McKeown, A., *Trans. Faraday Soc.*, **34**, 389 (1938).

¹¹⁹ Scheibe, G., *Ber.*, **59**, 2616 (1926); Morton, R. A., and Riding, K. W., *Proc. Roy. Soc.*, **113A**, 717 (1927); von Halban, H., and Eisenbrand, J., *Z. wiss. Phot.*, **25**, 149 (1928); Ley, H., and Volbert, F., *Ibid.*, **23**, 41 (1925); *Z. physik. Chem.*, **130**, 308 (1927); Eeckhout, J., *Naturw. Tijdschr.*, **17**, 72 (1935).

2060A, separated by a minimum at about 2600A. Krishnan and Guha¹²⁰ attribute the longer wave-length maximum to dissociation into nitrite ion and an oxygen atom and the second band to a similar dissociation producing an excited oxygen atom. Morton and Riding found that at concentrations greater than 0.025N, Beer's law fails, the band shifting in the direction of higher extinction coefficients, due to a superposed band which alone is present when very concentrated solutions are employed. Hantzsch and others have found that in concentrated nitric acid or in dilute solutions of nitric acid or alkyl nitrates in ether the band at 3100A is replaced by one at 2700A. This has been said to represent the absorption of a "pseudo-acid" form of nitric acid.¹²¹

Baudisch and Mayer¹²² observed that when aqueous solutions of potassium nitrate are exposed in a flat dish to the rays of a mercury lamp, oxygen is liberated, a blue coloration from starch and potassium iodide being produced in five to ten seconds. The interposition of a glass plate delays the change for twenty minutes. Warburg¹²³ made the first liquid-phase quantum yield determinations of the change of nitrates to nitrites. Since he observed that the photolysis proceeds much more rapidly in slightly alkaline than in neutral or in acid solutions, he employed solutions 0.00033 molar in sodium hydroxide. (This effect of pH was less apparent when more concentrated nitrate solutions were used.) In 0.33 molar potassium nitrate solutions the values of the quantum yield were 0.25 at 2070A, 0.17 at 2530A and 0.024 at 2820A. That the yields were low he explained by assuming that the efficiency of the dissociation is in some manner affected by the solvent. The fact that the yield decreases with increasing wave-length is readily interpreted by assuming that dissociation by larger quanta endows the dissociation products with sufficient kinetic energy to enable them more effectively to resist the imprisoning effect of surrounding solvent molecules which would tend to lower the quantum yields by inducing a recombination. Warburg also observed that for a given wave-length the quantum yield decreases with the concentration of the nitrate.

Anderson,¹²⁴ however, attempted to account for the low yields on the assumption that a reverse reaction may also occur, a "steady state" being reached when only a small portion of the nitrate had been decomposed. He supported this with the statement that the addition of small quantities of potassium nitrite partly or completely inhibited the photolysis of the nitrate. Villars¹²⁵ and also Vogels¹²⁶ found no evidence for the existence of a "steady state" in this reaction. The decomposition maintains a linear rate for at least 480 minutes. Warburg calculated on the basis of the then available thermochemical data that the energy required to split an oxygen atom from the nitrate ion corresponds to a wave-length between 2800 and 3150A. The observations of Villars and of Warburg (Figure 114) indicate, however, that the drop in quantum yield occurs at a wave-length corresponding to a quantum much larger than that just required to effect the

¹²⁰ Krishnan, K. S., and Guha, A. C., *Current Sci.*, **2**, 476 (1934); *Chem. Abs.*, **28**, 6370 (1934); *Proc. Indian Acad. Sci.*, **1A**, 242 (1934); *Chem. Abs.*, **29**, 1326 (1935).

¹²¹ See also Siegler-Soru, E., *Compt. rend.*, **183**, 1038 (1926). For absorption of the crystals, see Rodloff, G., *Z. Physik.*, **91**, 511 (1934).

¹²² Baudisch, O., and Mayer, E., *Ber.*, **45**, 1771 (1912); Baudisch, O., and Benford, F., *Naturwiss.*, **24**, 361 (1936).

¹²³ Warburg, E., *Sitz. Preuss. Akad. Wiss. Math. phys. Klasse*, 1228 (1918); *Chem. Abs.*, **14**, 1930 (1920); *Z. Elektrochem.*, **25**, 334 (1919).

¹²⁴ Anderson, W. T., Jr., *J. Am. Chem. Soc.*, **46**, 797 (1924).

¹²⁵ Villars, D. S., *J. Am. Chem. Soc.*, **49**, 326 (1927).

¹²⁶ Vogels, H., *Bull. sci. acad. roy. Belg.*, **22**, 320 (1936); *Chem. Abs.*, **30**, 6650 (1936); *Brit. Chem. Abs.*, **A**, 687 (1936).

decomposition. The explanation is probably to be found in the detailed mechanism of the recombination processes which occur in aqueous solution. Villars had difficulty in accounting for the fact that measurable quantum yields could be obtained by the use of the wave-length 3350Å, which he believed not to possess the requisite energy for dissociation. This difficulty has been removed by a more accurate knowledge of the heat of dissociation of oxygen, which makes the present value of the energy required for the decomposition correspond to about 3500Å.¹²⁷ Villars also made more precise the data on the effect of pH. In either polychromatic or monochromatic light of 2537Å the rates of decomposition increased at pH values slightly above 9 to maxima between 9 and 10, followed by relatively slight decreases at higher pH values. Vogels observed that the pH falls during photolysis, and that the rate may be accelerated by tartrates or, after a delay, by manganous salts.

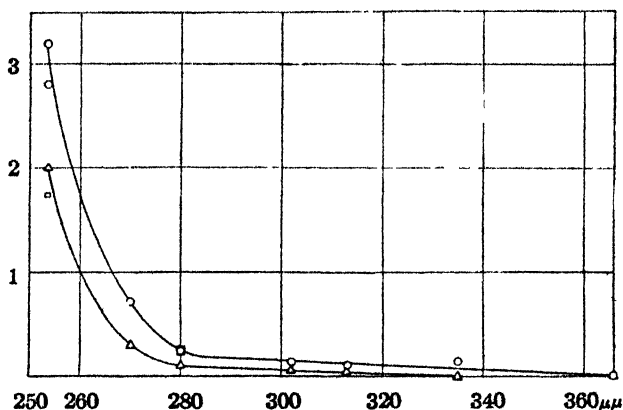


FIGURE 114. Quantum Efficiency of Monochromatic Light Absorbed by M. KNO₃. o = $\phi \times 10^3$ (buffered, pH 9.9). Δ = $\phi \times 10^2$ (unbuffered, pH 5.8). \square = $\phi \times 10$ (Warburg, KNO₃ 0.33 M, NaOH 0.0003M) where ϕ = moles transformed per quantum absorbed (Villars, *Journal American Chemical Society*).

Cultrera¹²⁸ finds that with mercury lamp irradiation, the reduction of nitrates may proceed to the formation of ammonia.

The decomposition of nitrate crystals appears to be confined to a surface layer not more than 20μ thick. At greater depths, recombination appears to be complete, since the oxygen cannot escape. Polarized rays with vibrations along the normal to the plane of the nitrate ions are much less effective than those with vibrations in the plane of the ions. In crystals, the wave-length threshold is much shorter, 2500Å.¹²⁹

Mercury nitrate also undergoes a photochemical change in aqueous solution, the sensitivity of the nitrate being increased by addition of alcohol or glycerol.¹³⁰ Fazal-ud-Din¹³¹ has stated that the reduction of solutions of a number of nitrates

¹²⁷ Note also Hymas, F. C., *J. Soc. Chem. Ind.*, **50**, 193T (1931).

¹²⁸ Cultrera, R., *Gazz. chim. ital.*, **66**, 440 (1936); *Chem. Abs.*, **31**, 3389 (1937); *Ann. stas. sper. agrar. Modena*, **5**, 163, 175 (1936); *Chem. Abs.*, **32**, 3266 (1938).

¹²⁹ Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, **3**, 417 (1935); *Brit. Chem. Abs.*, **A**, 682 (1935); *Trans. Faraday Soc.*, **31**, 1411 (1935).

¹³⁰ Shljivic, S., and Nicolice, D., *Bull. soc. chim. roy. Yougoslav.*, **6**, 159 (1936); *Chem. Abs.*, **30**, 4761 (1936); cf. Mudrovic, M., *Bull. soc. chim. roy. Yougoslav.*, **7**, 41 (1936).

¹³¹ Fazal-ud-Din, *Indian J. Agr. Sci.*, **6**, 844 (1936); *Chem. Abs.*, **30**, 8493 (1936); see also Rao, G. G., and Murty, K. S., *Proc. Natl. Inst. Sci. India*, **3**, 133 (1937); *Chem. Abs.*, **32**, 2028 (1938).

(1 mg. per cc.) can be brought about by sunlight although ultraviolet is more effective. This is in line with the data of Villars. Decomposition is said to be increased by the presence of reduced nickel or carbohydrates, but not to occur in the presence of zinc oxide.

The oxides N_2O_5 , TeO_3 and MoO_3 exhibit two regions of continuous absorption separated by a band of transmitted radiation.¹³² The first band, in each case, is interpreted as resulting from the separation of an oxygen atom in the 3P state from the molecule, and the second as resulting from the separation of an oxygen atom in the metastable 1D state. From the absorption of N_2O_5 the heat of dissociation of oxygen could be calculated to be 128 kcal, not far from the correct value of 117 kcal.

Other Nitrogen Compounds. That commercial sodium cyanide made from calcium cyanamide develops color in light and bleaches in darkness is attributed by Buchanan and Barsky¹³³ to a reversible photochemical reaction between cyanamide and a ferrocyanide, the latter being a contaminant.

Crystalline sodium azide is decomposed by wave-lengths below 4050A, the rate being directly proportional to the intensity.¹³⁴ The threshold for decomposition by bombardment with electrons lies at 11.65 volts. Obviously, no relation between these two thresholds is apparent.

Murarour¹³⁵ obtained only negative results in studying the effects of ultraviolet light, the alpha-rays from polonium, and x-rays on nitrogen iodide, picric acid, lead picrate, trinitrotoluene, nitrocellulose, nitroglycerin and *sym*-diethyldiphenylurea.¹³⁶

COMPOUNDS OF SULFUR

Exposure of a quartz reaction vessel containing sulfur, water and air to ultraviolet radiation results in the formation of various oxygen acids of sulfur. Dubrisay and Pallu¹³⁷ believe pentathionic acid to be the first product formed; this then slowly undergoes decomposition yielding sulfuric acid, sulfurous acid, sulfur and hydrogen sulfide.

The photochemical reaction between yellow arsenic and sulfur dissolved in carbon disulfide results in the formation of insoluble sulfides whose properties differ from those of known sulfides or of a mixture of the elements.¹³⁸

By irradiating mixtures of carbon disulfide and carbon tetrachloride in a Vitaglass screened mercury vapor lamp, Doran and Gillam¹³⁹ obtained a polymer of carbon monosulfide as a reddish-brown solid. Nicholes, Simmons and Crockford,¹⁴⁰ state that carbon disulfide is not decomposed by the 3660A line, but that the 2537A line, or a mercury arc in Pyrex leads to the formation of decomposition products including $(CS)_x$, C_3S_2 and a yellowish-brown solid $(C_3S_2)_x$.¹⁴¹

Sulfur dichloride absorbs strongly all wave-lengths shorter than 6200A. The

¹³² Dutta, A. K., and Gupta, P. K., *Proc. Roy. Soc.*, **139A**, 397 (1933).

¹³³ Buchanan, G. H., and Barsky, G., *Z. angew. Chem.*, **44**, 383 (1931).

¹³⁴ Müller, R. H., and Brous, G. C., *J. Chem. Physics*, **1**, 482 (1933).

¹³⁵ Murarour, H., *Bull. soc. Chim.*, **53**, 612 (1933).

¹³⁶ Mada, T. [Japanese P. 101,815, July 1, 1933], claims to prepare a nonhygroscopic sodium bicarbonate by raying with ultraviolet for about twenty minutes.

¹³⁷ Dubrisay, R., and Pallu, R., *Compt. rend.*, **193**, 339 (1931). See also Calcagni, G., *Gass. chim. ital.*, **65**, 558 (1936); *Chem. Abs.*, **30**, 384 (1936).

¹³⁸ Haenny, Ch., *Helv. Chim. Acta*, **13**, 725 (1930); *Chem. Abs.*, **25**, 643 (1931).

¹³⁹ Doran, W., and Gillam, A. E., *J. Soc. Chem. Ind.*, **47**, 259T (1928).

¹⁴⁰ Nicholes, P. M., Simmons, N. L., Jr., and Crockford, H. D., *J. Elsiha Mitchell Sci. Soc.*, **52**, 51 (1936); *Chem. Abs.*, **30**, 7457 (1936).

¹⁴¹ For the absorption spectrum of carbon disulfide, see Bruhat, G., and Pauthenier, M., *Compt. rend.*, **181**, 104 (1925); *J. Phys. Radium*, **6**, 287 (1925).

monochloride shows a strong maximum at 2660Å.¹⁴² The photochemical reaction between sulfur monochloride and chlorine has an induction period which may be lessened by substituting sunlight for diffused daylight. The rate of reaction is also greater in sunlight. The reaction may be catalyzed by antimony pentachloride.¹⁴³ Sulfur dichloride is one of the final products of the dissociation of sulfur monochloride by the action of light, S_2Cl_4 being an intermediate product.¹⁴⁴ When sulfur dichloride is heated or irradiated it undergoes changes in density, the course being that of a first order reaction. The velocity of reversion after irradiation is higher than after displacement by heat, probably because of the formation of a catalyst by the action of light.

Hydrogen Sulfide. Solutions of hydrogen sulfide in water and hexane have, according to Ley and Arends,¹⁴⁵ practically the same absorption curve, the maximum, at 1890Å, being attributed to undissociated molecules. Absorption at 2270Å in aqueous solutions was attributed to the HS^- ion. Warburg and Rump¹⁴⁶ found differences in the absorption curves in these solvents. Warburg found that in hexane the quantum yield for decomposition of hydrogen sulfide is 0.97 at 2070Å, 0.95 at 2220Å and 0.96 at 2530Å, the concentrations being 0.251, 0.1355 and 0.0452 molar. In aqueous solutions, however, the values were much lower, being 0.43 at 2070Å for 0.015 and 0.32 for 0.0369 molar solutions. At 2220Å, the yield was 0.32 and at 2530Å 0.22. Warburg pointed out that the difference might be due to the fact that hydrogen sulfide does not react with hexane but does react with water. He believed it possible to apply the Einstein law to solutions in which there is no interaction between photolyte and solvent but not to those in which there is such an interaction. An analysis from the standpoint of the influence which might be exerted by hydrated or solvated ions upon the recombination processes subsequent to the primary process does not seem to have been made as yet.

Sulfites. Albu and Goldfinger¹⁴⁷ have studied the absorption of the sulfite ion on the basis of the Franck-Haber theory of the electron-affinity spectrum of ions. Within the range 5000 to 1950Å the absorption spectrum depends only upon the pH and concentration of the solutions, and not on their age or method of preparation, provided autoxidation is prevented. The absorption of dissolved undissociated sulfur dioxide can be observed at pH 4 or lower. Absorption begins at 3270Å and has a maximum at 2800Å. The spectrum of the sulfite ion SO_3^{--} , a structureless electron-affinity spectrum, may be observed in solutions of pH greater than 6. The sulfite ion spectrum has a long wave-length limit of 2660Å and corresponds to the process:¹⁴⁸ $SO_3^{--}(H_2O) + h\nu \rightarrow SO_3^- + H + OH^-$. The Franck-Haber theory predicts that the corresponding electron-affinity spectrum of the bisulfite ion should be 1.5 to 2 e-volts to the short wave-length side of that of the sulfite ion. In agreement with this prediction, there was found to be no absorption by the bisulfite ion at wave-lengths greater than 2250Å. The long wave-length limits of the absorption by the $S_2O_8^{--}$ and $S_2O_6^{--}$ ions are 2700 and 2600Å, respectively. No absorption by the sulfate ion could be detected. Haber and Wansbrough-

¹⁴² Lowry, T. M., and Jessop, G., *J. Chem. Soc.*, 1421 (1929); Lorenz, L., and Samuel, R., *Z. physik. Chem.*, **14B**, 219 (1931).

¹⁴³ Bothamley, R. P., *Trans. Faraday Soc.*, **24**, 47 (1928).

¹⁴⁴ Spong, A. H., *J. Chem. Soc.*, 485 (1934).

¹⁴⁵ Ley, H., and Arends, B., *Z. physik. Chem.*, **15B**, 311 (1932).

¹⁴⁶ Warburg, E., and Rump, W., *Z. Physik*, **58**, 291 (1930). Studies in dichloromethane, chloroform and carbon tetrachloride as solvents are due to Avery, W. H., and Forbes, G. S., *J. Am. Chem. Soc.*, **60**, 1005 (1938).

¹⁴⁷ Albu, H. W., and Goldfinger, P., *Z. physik. Chem.*, **16B**, 338 (1932).

¹⁴⁸ See for another interpretation, Farkas, L., and Farkas, A., *Trans. Faraday Soc.*, **34**, 1113 (1938).

Jones¹⁴⁹ have studied the photochemical reaction which (in the absence of oxygen) occurs subsequent to the primary process postulated above. As secondary reactions there might be expected a combination of the hydrogen atoms to molecular hydrogen and a combination of two SO_3^- ions into a dithionate ion $\text{S}_2\text{O}_8^{--}$. The quantum yields were, however, very small for the formation of dithionate ions, being about 0.07 at pH 9 and decreasing at greater alkalinities. Instead, the majority of the SO_3^- ions formed in the primary process combine with hydrogen atoms to form bisulfite ions.

In the presence of air, ultraviolet (2300-2800Å) accelerates the thermal oxidation of sodium sulfite. A 0.2*N* solution of sodium sulfite is completely oxidized in light in about three hours. A particularly interesting feature is the inhibiting effect of small quantities of various substances. According to Mathews and Dewey¹⁵⁰ pyridine strongly inhibited the process when present in the concentration of 5 cc. per liter. Methyl and ethyl acetate had a much weaker effect. Five drops of benzaldehyde per liter strongly inhibited the reaction but the same amount of glycerol produced only a slight effect. Urea had no effect. Hydroquinone and phenol were effective but not as much so as quinine sulfate. Sucrose (0.025*N*) produced less inhibition than did phenol (0.001*N*).¹⁵¹

Bäckström¹⁵² reported a series of investigations on the behavior of inhibitors, particularly alcohols, which did much to explain the nature of the photochemical oxidation and of the thermal one as well. It was shown that the photochemical process is a chain reaction, the quantum yields in the absence of inhibitors corresponding to an uptake of about 50,000 molecules of oxygen per quantum absorbed. Since in general, the inhibitors of the photochemical reaction also inhibited the thermal one, it followed that the latter was a chain reaction as well. The role of the inhibitor in both cases consists in the breaking of chains, probably by an induced reaction between the inhibitor and one of the reactants. Attention was devoted to the mechanism of the inhibition and to the length of the chains when broken rather than to the nature of the chains, since the work was done before the theory of the electron affinity spectrum had been developed.

The rates of the light and dark reactions could be represented by the formulas:

$$V_{\text{light}} = k_0 v_{\text{dark}} \quad \text{and} \quad V_{\text{dark}} = \frac{k_1}{kC + k_2}$$

in which k_1 , k_2 and k_3 are constants applicable to all alcohols as inhibitors, k is a specific constant for each inhibitor and C is the concentration of the inhibitor. The form of the equations suggested that the presence of the alcohols did not affect the rate of starting the chains so that the inhibitors function solely by breaking the chains. The constant k_2 indicates that some chains may be broken by processes independent of the presence of added inhibitor. In the case of the thermal reaction it was shown that the alcohols were oxidized in breaking the chains. The amount of oxidation of alcohols could be determined by colorimetric measurements of the aldehydes and ketones produced. At low inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concen-

¹⁴⁹ Haber, F., and Wansbrough-Jones, O. H., *Z. physik. Chem.*, **18B**, 103 (1932).

¹⁵⁰ Mathews, J. H., and Dewey, L. H., *Eighth Intern. Congr. Appl. Chem., Sect. IX, Orig. Comm.*, **20**, 247 (1912); *J. Am. Chem. Soc.*, **39**, 635 (1917).

¹⁵¹ Mathews, J. H., and Mason, R. B., *J. Phys. Chem.*, **30**, 414 (1926) later erroneously stated the phenols to act as positive catalysts.

¹⁵² Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927); *Medd. Kgl. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927); Bäckström, H., and Alyea, H. N., *J. Am. Chem. Soc.*, **51**, 90 (1929).

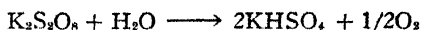
tration. At high inhibitor concentrations the amount of alcohol oxidized per unit time is constant, and independent of concentration, in either the thermal or photochemical oxidation. Over a considerable range of high inhibitor (isopropyl alcohol) concentrations, the product of the rate of sulfite oxidation and inhibitor remained constant, and the ratio between this product and the amount of acetone formed was the same, 74 to 77, in the thermal and in the photochemical oxidations. From this it followed that in a solution of a given composition the chain length is the same whether the chains are formed thermally or photochemically.

A solution 0.1*M* with respect to benzyl alcohol gave a quantum yield of 64 molecules of oxygen or 128 of sulfite reacting per quantum. From the amount of acetone formed it was determined that the number of molecules of sulfite oxidized for each molecule of alcohol oxidized was 58, of the same order of magnitude. This indicates that in the process of breaking a reaction chain, 2.2 molecules of the alcohol are oxidized. In other words, the induced oxidation of benzyl alcohol has a quantum yield of 2.2. It was later found by Bäckström¹⁵³ that light intensity enters into the rate equation as approximately the half power, both in the numerator and in an additional term in the denominator. The reaction had a pH dependence which suggested that both sulfite and bisulfite ions must be concerned in the mechanism. When oxidation occurs, the primary SO_3^- probably forms an intermediary SO_5^- ion which dehydrogenates the bisulfite ion, present at the effective pH, producing a sulfate ion and reforming the SO_3^- ion which can again be oxidized. The inhibiting action of the alcohol is due to its induced oxidation, probably by the assumed SO_5^- ion.

Allmand and Maddison¹⁵⁴ believed that light of ordinary wave-lengths has no effect on the rate of oxidation of sodium sulfite in solution. Titoff¹⁵⁵ found that copper sulfate is without effect upon the ultraviolet reaction, but catalyzes the reaction in ordinary light. Franck and Haber¹⁵⁶ postulate that the effect of the copper ion is to start the thermal reaction by forming the ion SO_4^- the same ion as that later found by Bäckström to be the primary product in the photo-reaction.¹⁵⁷

Persulfates. That aqueous solutions of potassium persulfate are light-sensitive was demonstrated by Dhar¹⁵⁸ and Elbs and Neher.¹⁵⁹

In a series of investigations, Morgan and Crist¹⁶⁰ found that the reaction could be expressed by the equation:



In very dilute solutions, the order of reaction was unimolecular, as is the thermal reaction which occurs at higher temperatures. In concentrated solutions which absorbed all the light, the reaction was of zero order. Increasing the oxygen

¹⁵³ Bäckström, H., *Z. physik. Chem.*, **25B**, 122 (1934).

¹⁵⁴ Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (1927).

¹⁵⁵ Titoff, A., *Z. physik. Chem.*, **45**, 641 (1903).

¹⁵⁶ Franck, J., and Haber, F., *Sitzber. Preuss. Akad. Wiss.*, 250 (1931); see also Albu, H. W., and von Schweinitz, H. D., *Ber.*, **65B**, 729 (1932).

¹⁵⁷ There have from time to time been efforts to employ ultraviolet light in the preparation of sulfuric acid. Kühne, H., French P. 393,461, 1908; *J. Soc. Chem. Ind.*, **28**, 90 (1909); British P. 17,520, 1908; *J. Soc. Chem. Ind.*, **28**, 982 (1909). German P. 203,541; Chmura, T., *Chem. Age*, **13**, 327,307 (1925); British P. 237,257; de Sotto, G. E., British P. 265,857, July 20, 1926. No practical applications have been made.

¹⁵⁸ Dhar, N. R., *Proc. Akad. Vetensk.*, **23**, 308 (1920).

¹⁵⁹ Elbs, K., and Neher, P., *Chem. Z.*, **45**, 1113 (1921).

¹⁶⁰ Morgan, J. L. R., and Crist, R. H., *J. Am. Chem. Soc.*, **49**, 16, 338, 960 (1927).

concentration did not reverse the reaction. Hydrogen and nitrogen appeared to exhibit an accelerating effect. Potassium persulfate absorbs only wave-lengths shorter than about 2500A in a 0.01M solution and 3000A in a 0.1M solution. The upper limit of the radiations effective in producing the decomposition was probably at about 2900A and the maximum sensitivity at about 2300A. The reaction was proportional to the light intensity, and the temperature coefficient was 1.18, compared with about 3 for the thermal reaction. The rate of reaction was retarded by the addition of potassium hydroxide, potassium sulfate or sulfuric acid. The retardation was not due to internal filtering, was hyperbolic and seemed to be of the same general nature in the presence of various added electrolytes. The quantum efficiency was unity in 0.05 molar neutral or alkaline solutions, the wave-lengths used being 2540, 2650 and 3020A.¹⁶¹ In acid solutions the values of the quantum yield are somewhat reduced. Solid potassium persulfate is also decomposed by ultraviolet light.

Marmier¹⁶² has reported that decomposition of aqueous solutions of sodium thiosulfate results in the formation of sulfur and hydrosulfite. The latter was rapidly decomposed by ultraviolet and after an exposure of 75 minutes under the conditions of observation no traces remained.

Ammonium Thiocyanate. Holmes¹⁶³ observed that freshly prepared concentrated solutions of ammonium thiocyanate exposed to ultraviolet light in glass containers evolved a gas and developed a reddish color which soon faded. In quartz containers, sulfur separated from the solution. Werner and Bailey¹⁶⁴ suggested that the photoreaction involved only the production of ammonia and thiocyanic acid, the color being due to traces of iron as impurity. This theory was corroborated by Patten and Smith.¹⁶⁵ According to these investigators, light accelerates oxidation of the iron so that the latter can react with the thiocyanate. Wave-lengths less than 5400A produced the coloration, those between 4000 and 4300A being the most effective. Sharma¹⁶⁶ considered the color to be due to a loose additive complex of ferrous thiocyanate with oxygen.

Shorter wave-lengths (3000-1850A) can decompose thiocyanates of ammonium, sodium or potassium with liberation of sulfur, according to Jablczynski and Jablczynska.¹⁶⁷ The reaction is believed to be reversed in the dark.

The velocity of solution of amorphous selenium is increased by light but that of monoclinic selenium is not affected.¹⁶⁸

ARSENIC AND ANTIMONY COMPOUNDS

An account of the investigations on the source of the glow of arsenic at high temperatures is beyond the scope of this work.¹⁶⁹ Lead arsenite is photosensitive. When dried in an air-bath in the dark, it remains white, but when exposed to light

¹⁶¹ Crist, R. H., *J. Am. Chem. Soc.*, **54**, 3939 (1932).

¹⁶² Marmier, L., *Compt. rend.*, **154**, 32 (1912).

¹⁶³ Holmes, M., *J. Chem. Soc.*, 1690 (1926).

¹⁶⁴ Werner, E. A., and Bailey, K. C., *J. Chem. Soc.*, 2970 (1926); more complicated theories of the origin of the color were suggested by Holmes, M., and by Bhatnagar, S., Dunncliffe, H., and Ali, M., *J. Indian Chem. Soc.*, **4**, 229 (1927).

¹⁶⁵ Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada*, **22**, 221 (1928).

¹⁶⁶ Sharma, B. S., *J. Chem. Soc.*, 308 (1930); see also Rao, S. V., *J. Chem. Soc.*, 880 (1934).

¹⁶⁷ Jablczynski, K., and Jablczynska, H., *Roczniki Chem.*, **10**, 579 (1930); *Chem. Abs.*, **25**, 877 (1931).

¹⁶⁸ Shidei, J., Hashizuma, S., and Kitahara, S., *Bull. Chem. Soc. Japan*, **10**, 374 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935); Sterzel, S. E., and Afzelius, I., *Svensk Kem. Tidskr.*, **49**, 281 (1937); *Brit. Chem. Abs.*, **A** (1), 90 (1938).

¹⁶⁹ Emeléus, H. J., *J. Chem. Soc.*, 783 (1927). For phosphorus, Emeléus, H. J., *Nature*, **115**, 460 (1925); *J. Chem. Soc.*, 1336 (1926); Emeléus, H. J., and Purcell, R. H., *J. Chem. Soc.*, 788 (1927); Petrakal, A., *Naturwiss.*, **16**, 205 (1928); Miller, C. C., *J. Chem. Soc.*, 1823, 1829 (1929).

it turns brown. Mixed with gelatin and applied to paper and dried in the dark, it can be used in photography, developing warm sepia tones when exposed under a negative. Not all samples of lead arsenite possess this property. No other metallic arsenites are light-sensitive.¹⁷⁰

Detailed determinations have been made by Weigel¹⁷¹ of the absorption of light and the electrical conductivity of realgar when the crystal is exposed to light of various wave-lengths. Fragments of realgar exposed to direct sunlight for 112 hours behind sheets of glass of various colors showed the greatest change with a green glass of maximum transparency near 520μ .

Solutions of antimony oxide in hydrochloric or tartaric acids and of antimony trichloride in saturated sodium chloride solution in ordinary glass vessels are photochemically oxidizable by sunlight.¹⁷² Light of shorter wave-length is required in the case of solutions of antimony trioxide or of tartar emetic in sulfuric acid, or of antimony trichloride in carbon tetrachloride and in saturated calcium chloride solution. The amount of oxidation depends on the kind of solution, wave-length and intensity of the radiation and concentrations of antimony and of oxygen.

In carbon disulfide, white phosphorus is converted by light into red phosphorus, a dissociation and recombination being involved.¹⁷³

When boron hydride, B_4H_{10} , is kept over mercury at room temperature, it slowly undergoes decomposition with the formation of the hydride, B_2H_6 . The decomposition is accelerated greatly by ultraviolet rays, but not by sunlight.¹⁷⁴

METALS AND SALTS

Under the influence of light, copper combines with chlorine¹⁷⁵ but not with bromine or iodine; with oxygen, but not with sulfur; with water, but not with hydrogen sulfide; with ammonia, but not with phosphine or arsine. Aqueous solutions of the chlorides or sulfates of gold, silver, uranium, copper, nickel, chromium and cobalt were reported by Berthelot and Gaudechon¹⁷⁶ to be unaffected by ultraviolet radiation. The sulfates of nickel and cobalt gave a slight brown precipitate, attributed to the presence of traces of iron. Solutions of ferrous sulfate gave a precipitate of the basic salt. Pure ferric sulfate did not give a precipitate but in the presence of nickel or cobalt sulfate precipitated the basic salt. Urbain and Scal¹⁷⁷ stated that the passage of rays (from an arc) through tetrachlorides of titanium, tin, or carbon, caused a marked decomposition, chlorine being liberated.

A method of depositing metals has been advocated by Jacquier.¹⁷⁸ The process comprises precipitating metals from solutions of their salts by treatment with ultraviolet rays in the presence of aluminum. Mercury vapor lamps are suspended between aluminum plates in the tank containing the solution to be treated.

Light is believed to facilitate the reduction of some metallic oxides. Actinic rays are said to promote the interaction of oxygenated compounds (e.g., calcium phosphate), barytes or bauxite with chlorine in the presence of a reducing

¹⁷⁰ Reissaus, G. C., *Z. angew. Chem.*, **44**, 959 (1931).

¹⁷¹ Weigel, O., *Tech. Min. Petr. Mitt.*, **38**, 288 (1925); *Chem. Abs.*, **20**, 3268 (1926)

¹⁷² Brüll, W., with Schlagel, H., *Z. anorg. Chem.*, **217**, 401 (1934).

¹⁷³ Rathenau, G., *Physica*, **4**, 503 (1937), *Chem. Abs.*, **31**, 6560 (1937).

¹⁷⁴ Stock, A., and Friederici, K., *Ber.*, **46**, 1959 (1913).

¹⁷⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 129 (1915)

¹⁷⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).

¹⁷⁷ Urbain, E., and Scal, C., *Compt. rend.*, **168**, 887 (1919).

¹⁷⁸ Jacquier, G., *British P.* 17,790, Aug. 2, 1913.

agent such as carbon. At temperatures between 200° and 1000°C., inorganic halides are said to be secured.¹⁷⁹

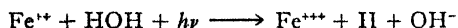
The yellow amorphous modification of indium oxide is sensitive to light when in the presence of some reducing agents as benzaldehyde. The color of the oxide changes from gray to dark gray or black. Also, some reduction products are formed. Selenium oxide is not sensitive under the same conditions.¹⁸⁰

Krauss and Gerlach¹⁸¹ found that the preparation of iridium halides by the action of the halogens upon iridium or its hydroxide could be hastened by the action of light.

Hibben¹⁸² observed that some large crystals of magnesia became tinted a deep purple on exposure to the 2537A line. On removal from the light, spontaneous decolorization occurred in several weeks at 25°C., or in three minutes at 1000°C. It was accompanied by emission of light throughout the visible spectrum. The first effect was ascribed to a type of electron migration, and the later effects to a recombination. It may be related to the presence of impurities since not all crystals behave alike. The 4358A line decolorized the purple crystals in thirty minutes.¹⁸³

Light from a carbon arc accelerates the rate of evolution of hydrogen from dilute sodium and potassium amalgams in water.¹⁸⁴

Iron Salts. That ferrous hydroxide and sulfate are more rapidly oxidized in light than in darkness was first made known by Chastaing.¹⁸⁵ The ferrous ion when irradiated with wave-lengths shorter than 2900A, is oxidized to ferric ion and hydrogen is evolved.



The quantum yield in aqueous solution is 0.05. The primary process is followed by a combination of two hydrogen atoms, which occurs in competition with the reverse reaction. The activation energy of the latter is 7 kcal.¹⁸⁶

The color of hydrochloric acid solutions of ferric chloride increases on exposure to sunlight or other sources of intense light.¹⁸⁷ On removal from the light, the solutions slowly return to their original condition. Increased light absorption also results from heating a solution of ferric chloride. A crystal of ferric chloride shows, in addition to general absorption starting at 5000A, a sharp band at 6200A, from 50 to 100A in width.¹⁸⁸

In alcoholic solution, ferric chloride is readily bleached in light by reduction to the ferrous salt, a reaction discovered by Bestucheff in 1725.¹⁸⁹ The reaction is best conducted in the presence of organic substances, either as solvent or added to the solution, or bound in complex form to the iron, since these organic compounds can be oxidized by or react with the chlorine liberated in the photochemical decomposition. A wide variety of organic reducing agents have been studied,

¹⁷⁹ British P. 302,927, Dec. 22, 1927, to Naamlooze Vennootschap Elektrochemische Industrie; *Chem. Abs.*, 23, 4304 (1929).

¹⁸⁰ Renz, C., *Helv. Chim. Acta*, 15, 839 (1932); *Chem. Abs.*, 26, 4754 (1932).

¹⁸¹ Krauss, F., and Gerlach, H., *Z. anorg. allgem. Chem.*, 147, 265 (1925).

¹⁸² Hibben, J. H., *Phys. Rev.*, 51, 530 (1937).

¹⁸³ For effects of visible light and x-rays on lead oxides, see Hoffmann, J., *Z. anorg. Chem.*, 228, 160 (1936).

¹⁸⁴ Bhatnagar, S. S., Prasad, M., and Mukerji, D. M., *Quart. J. Indian Chem. Soc.*, 1, 263 (1925); *Chem. Abs.*, 19, 3429 (1925).

¹⁸⁵ Chastaing, P., *Ann. Chem.*, 10, 145 (1877).

¹⁸⁶ Potterill, R. H., Walker, O. J., and Weiss, J., *Proc. Roy. Soc.*, A156, 561 (1936).

¹⁸⁷ Ritchie, K. S., *J. Phys. Chem.*, 32, 1269 (1928).

¹⁸⁸ Rawlins, F., and Snow, C. P., *Z. Krist.*, 83, 41 (1932).

¹⁸⁹ Plotnikow, J., "Allgemeine Photochemie," p. 410. Berlin, de Gruyter, 1936.

including paper, glycerol, and many acids. It was as a result of the study of this reaction that Grotthuss evolved the law which bears his name.¹⁹⁰ Winther¹⁹¹ found that aqueous solutions of ferric chloride, when free from organic matter, undergo only a very slight reaction. Puxeddu¹⁹² reported that the reaction in absolute ether follows a monomolecular course. At the end of reaction, the ether was partially chlorinated.

Prasad and Sohoni¹⁹³ studied the influence of temperature, light intensity, water and neutral salts on the decomposition of ferric chloride in alcoholic solution. The temperature coefficient is 1.0 to 1.15. In anhydrous solution a steady state is apparently reached, the reaction being reversible. Small amounts of water increase the initial rate of the reaction but seem to decrease the total amount of reduction. Minute quantities of the chlorides of magnesium or the alkalis are strongly inhibiting. Variations of light intensity have a more pronounced influence on the rate of the reduction in dilute solutions than in more concentrated ones. The quantum yield varies from 0.6 to 4 in various alcohols, including methyl, ethyl, propyl and butyl.¹⁹⁴ The quantum yield increases with the concentration of the ferric chloride, the frequency of the light and the temperature. These workers find the products to be ferrous chloride and chlorine, no side reactions occurring within the first two hours. In later work, it was observed that in dilute solutions, two reactions may take place, each of zero order.¹⁹⁵ The initial velocity of the reduction in dilute solutions is proportional to a power of the concentration, which depends on the nature of the solvent. In concentrated solutions, however, the initial velocity is independent of the concentration of the ferric chloride. It was believed unlikely that the primary process involved a photodissociation.¹⁹⁶ There may be either an activation of ferric ions which then react with the alcohols, or an activation of a molecule of ferric chloride, which then reacts with a second molecule to yield ferrous chloride and chlorine, the latter attacking the alcohols. Either mechanism would give a quantum yield of two.

In studying the influence of light upon the decomposition of ferric iron preparations containing citric acid, a decomposition which sometimes causes the stoppers to be blown from bottles by the accumulation of carbon dioxide, Fry and Gerwe¹⁹⁷ reviewed the work on the reduction of ferric salts by organic acids in light. Eder¹⁹⁸ and de Vries¹⁹⁹ found ordinary light to effect the reduction of ferric salts in the presence of oxalic, citric and malic acids. A small amount of ferric chloride oxidized a great excess of acid. Neuberg²⁰⁰ made an extensive study of the action of both sunlight and ultraviolet light upon sixty substances in the presence of ferric salts and uranic salts. Fry and Gerwe found that three moles of carbon dioxide were produced for each molecule of ferric sulfate reduced. No

¹⁹⁰ Ross, W. H., *J. Am. Chem. Soc.*, **28**, 790 (1906); Schneider, M., *Z. physik. chem. Unterrichts.*, **39**, 271 (1927); Benrath, A., *Z. physik. Chem.*, **74**, 115 (1910); Ghosh, J. C., and Mitra, B. N., *J. Indian Chem. Soc.*, **5**, 191 (1928); *Chem. Abs.*, **23**, 21 (1929).

¹⁹¹ Winther, C., *Z. Elektrochem.*, **18**, 138 (1912); *Z. wiss. Phot.*, **11**, 60 (1912); **9**, 205 (1910).

¹⁹² Puxeddu, E., *Gazz. chim. ital.*, **50**, 154 (1920); **52**, 229 (1922).

¹⁹³ Prasad, M., and Sohoni, N. V., *J. Indian Chem. Soc.*, **8**, 489 (1931); *Chem. Abs.*, **26**, 378 (1932).

¹⁹⁴ Prasad, M., and Limaye, P. S., *J. Indian Chem. Soc.*, **10**, 91, 101 (1933); *Chem. Abs.*, **27**, 3882 (1933).

¹⁹⁵ Prasad, M., and Mohile, B. V., *Proc. Natl. Acad. Sci. India*, **6**, 261 (1936); *Chem. Abs.*, **31**, 1298 (1937).

¹⁹⁶ Prasad, M., Mohile, B. V., and Nigudkar, K. D., *J. Univ. Bombay*, **5**, Pt. 2, 142 (1936); *Chem. Abs.*, **31**, 3790 (1937).

¹⁹⁷ Fry, H. S., and Gerwe, E. G., *Ind. Eng. Chem.*, **20**, 1392 (1928).

¹⁹⁸ Eder, J. M., *Monatsh.*, **1**, 755 (1880); *Ber.*, **14**, 1183 (1881).

¹⁹⁹ de Vries, H., *Rec. trav. Chim.*, **3**, 365 (1884); *Chem. Zentr.*, **56**, 219 (1885).

²⁰⁰ Neuberg, C., *Biochem. Z.*, **44**, 495 (1912).

carbon monoxide formed. They proposed a mechanism in which the citric acid is converted into hydrogen, carbon dioxide and acetone-dicarboxylic acid. The latter immediately decomposed to yield a second molecule of carbon dioxide and acetoacetic acid, which in turn, yielded a third molecule of carbon dioxide and acetone. The ferric sulfate was believed to aid the oxidation of the hydrogen formed in the first reaction. The summation of the reactions gave the stoichiometrical ratio between ferric sulfate reduced and carbon dioxide produced which was found experimentally. It is to be noted that the sequence of events was stated to depend upon an action of the light directly upon the citric acid rather than upon the ferric salt. From the preceding discussion, it is evident, however, that in most cases in which ferric salts are photochemically reduced in the presence of organic matter, the light acts primarily upon the ferric salt. Lal and Ganguli²⁰¹ reported that the rate of reduction of ferric salts in the presence of a mercury arc as source was proportional to the light intensity. Reduction was strongly accelerated by traces of thorium, uranium, copper and zirconium salts.²⁰²

Ferrocyanides and Other Complex Salts. A reversible color change occurs in solutions of potassium ferrocyanide in sealed tubes exposed to light. Only after months is there some precipitation of ferrous hydroxide.²⁰³ Equilibrium conditions for a 0.25-per cent solution of potassium ferrocyanide in water are reached after an exposure of thirty minutes to an arc.²⁰⁴ With exposures of sixty minutes, the percentage decomposition decreased from 0.23 per cent to 0.10 per cent as the concentration of the salt was decreased from 7.67 to 3.07 gm. per 100 cc. A further decrease in the concentration of the salt to 1.53 gm. per 100 cc. resulted in an increase in the decomposition to 0.40 per cent. Up to a certain amount, the presence of potassium hydroxide aids the decomposition, but larger amounts decrease decomposition to the value found for neutral solutions. Complete reversibility of the reaction was shown after the first exposure to light and darkness, but with successive equal exposures the amount of decomposition increased, and the reversibility of the reaction decreased. Baur²⁰⁵ found oxygen to accentuate the darkening in color of ferrocyanide solutions on illumination, although darkening occurs also with deaerated freshly prepared solutions. In acid solutions, Prussian blue forms. If the ferrocyanide solution is passed through a column of granulated aluminum, the original yellow color disappears, and the solution ceases to be photochemically sensitive. These facts were interpreted as indicating that the ferrocyanide ion itself is photochemically insensitive, the light reaction being due to the photodecomposition of the ferricyanide ion always present in small quantities.

Baudisch²⁰⁶ observed that ferrous ions, as well as pentacyanoaquoferrite ions, are produced when solutions of potassium ferrocyanide, neutral or feebly acid with carbonic acid, are exposed to the carbon arc or to direct sunlight in the absence of air. In the presence of air and light, the yellow ferrite ions are immediately oxidized to the dark violet pentacyanoaquoferrate ions, which react with the first named ions to form complex compounds that have a pale yellow color. The

²⁰¹ Lal, P., and Ganguli, P. B., *Z. anorg. allgem. Chem.*, **229**, 16 (1936).

²⁰² See also Burt, J. B., *J. Am. Pharm. Assn.*, **17**, 650 (1928) and Purkayastha, R. M., *J. Indian Chem. Soc.*, **9**, 237 (1932).

²⁰³ Baudisch, O., and Bass, L., *Ber.*, **55B**, 2698 (1922); *Chem. Abs.*, **16**, 4137 (1922) For the absorption spectra, see Plotnikow, J., and Karschulin, M., *Z. Elektrochem.*, **33**, 212 (1927); Getman, F., *J. Phys. Chem.*, **32**, 187 (1928); Briggs, S., *J. Chem. Soc.*, **99**, 1019 (1911); **117**, 1026 (1920); *J. Phys. Chem.*, **32**, 1422 (1928).

²⁰⁴ Rossi, G., and Bocchi, C., *Gazz. chim. ital.*, **55**, 876 (1925).

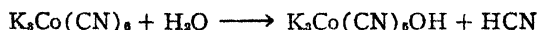
²⁰⁵ Baur, E., *Helv. Chim. Acta*, **8**, 403 (1925).

²⁰⁶ Baudisch, O., *Ber.*, **62B**, 2706 (1929).

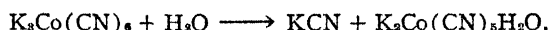
presence of sodium azide inhibits the formation of these products, and under these conditions the yellow potassium ferrocyanide is oxidized directly to the dark violet potassium pentacyanoaquoferate ion. In an air-free system, the iron atom of potassium ferrocyanide is activated by light in consequence of the mobilization of its secondary valences. The original inactive compound is rapidly reformed in the dark. In the presence of air and light, peroxo-compounds possessing unusual oxidizing powers are produced in addition to the usual ferric and ferrous complex ions.

Dickinson and Ravitz²⁰⁷ state that systems containing the ferro- and ferricyanide ions together with the iodide ion and iodine, are sensitive to light not absorbed by the complex cyanides. When light was directed into such an equilibrium mixture, the concentration of titratable iodine increased. The photochemical reaction was believed to be a reduction of ferricyanide to ferrocyanide by iodide, the absorption being almost entirely by the tri-iodide ion. One molecule of iodine was formed for each quantum absorbed. In discussing the possible mechanism of the reaction, these authors suggested the possibility that an iodine atom might react with an iodide ion to produce the ion I_2^- which might then serve as the reducing agent for the ferricyanide.

It is the opinion of Schwarz and Tede²⁰⁸ that potassium ferricyanide is not appreciably sensitive to light, decomposition taking place to a very slight extent after intense illumination. The change consists in hydrolysis to aquo-complex salts and ultimately ferric hydroxide, and also in the oxidation of hydrocyanic acid to cyanogen with the production of potassium ferrocyanide. In the case of potassium cobaltcyanide, the reaction is



and



The corresponding chromium compound behaves similarly to the cobaltcyanide, but the manganese compound is rapidly decomposed in the absence of light into manganic hydroxide, hydrocyanic acid and potassium cyanide.²⁰⁹

Pavolini²¹⁰ observed that when paper is coated with a solution of 5-per cent potassium ferricyanide and 5-per cent ammonium molybdate, a print can be made on exposure to sunlight. The exposed print can be fixed in water acidulated with 1-per cent hydrochloric acid. If, on the other hand, these compounds are added to a gelatin or gum arabic solution, the gelatin is rendered insoluble by the decomposition products formed on exposure to light. This mixture produces the same result as do dichromates.

A weak source of light is capable of increasing by about 10 per cent the rate of oxidation of hydrazine by the ferricyanide ion. The effective rays are those absorbed by the ferricyanide.²¹¹

An aqueous solution of sodium nitroprusside when exposed to sunlight in an open vessel is decomposed into hydrogen cyanide, sodium nitrite and $Na_2Fe_2(CN)_6$, the latter, in the presence of sodium hydroxide, being converted into Prussian

²⁰⁷ Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52**, 4770 (1930).

²⁰⁸ Schwarz, R., and Tede, K., *Ber.*, **60**, 69 (1927).

²⁰⁹ For observations on sodium nitroferrocyanide, see Justin-Mueller, E., *Bull. soc. chim.*, **2**, 1932 (1935).

²¹⁰ Pavolini, T., *Corr. fot.*, **26**, 723 (1929); *Chem. Abs.*, **24**, 2958 (1930).

²¹¹ Gilbert, E. C., *J. Phys. Chem.*, **35**, 3631 (1931).

blue.²¹² If the exposure to sunlight takes place in a closed vessel, nitric oxide is evolved.

The precipitates formed on mixing a concentrated aqueous solution of sodium nitroprusside with aqueous solutions of silver nitrate, mercuric nitrate, or ferrous sulfate, suffer change after exposure to sunlight for ten minutes.²¹³

Potassium permanganate and potassium dichromate are very stable towards ultraviolet light.²¹⁴

Although the chromates of ammonium, potassium and sodium are unaffected by sunlight in the absence of substances capable of oxidation, in the presence of such substances the photochemical reduction of the chromates and dichromates occurs rapidly under the radiations of an arc light.²¹⁵ The reduction results in either a brownish precipitate or a green solution according to the properties of the substance which serves as reducing agent. In some cases there is an evolution of gas, either ammonia, in the case of ammonium chromates, or carbon dioxide. According to Bhattacharya and Dhar,²¹⁶ the orders of the reactions between chromic acid and the following acids in sunlight and in darkness are, respectively: citric acid, 2, 2.5; tartaric acid, 2, 3; lactic acid, 3, 3. Manganous sulfate accelerates most of the reactions and, except in the case of tartaric acid, reduces the order. With decrease in the order of the reaction, the temperature coefficients of the velocity coefficients usually rise. The temperature coefficient for the photochemical reaction is always greater than unity but less than that of the dark reaction with the same acid. In all cases, several molecules react for each quantum absorbed, the number increasing with increase in the concentration and with the temperature. The rate of reaction with or without manganous sulfate is directly proportional to the intensity of the incident radiation, except in the reactions with citric and tartaric acids in the absence of manganous sulfate, the rates of which are proportional to the square root of the intensity of the radiation.

Forbes and Leighton²¹⁷ electrolyzed 0.006 to 0.05N chromate solutions in normal and three normal sulfuric acid between platinum electrodes at various current densities, comparing the yields obtained in the light of a 1500-watt quartz mercury arc and in darkness. At an illuminated cathode, a 0.5 per cent greater efficiency was observed. Part or all of the increased efficiency could be attributed to local heating in a thin diffusion layer at the cathode. An absence of any increase in yield in light would be compatible with the existence of light-sensitive chromate if the latter is equally reactive electrochemically before and after photoexcitation. Granting, however, that the slightly greater electrochemical efficiency in light may be due in part to excited chromate, it would be impossible to estimate the quantum yield without making certain assumptions, especially one regarding the life of the excited molecule, upon which would depend its chance of reaching the cathode.

²¹² Justin-Mueller, E., *Bull. soc. chem.*, **2**, 1932 (1935).

²¹³ Leffmann, H., and Pines, C. C., *Bull. Wagner Free Inst.*, **4**, 41 (1929); *Brit. Chem. Abs.*, **A**, 1431 (1929).

²¹⁴ Mathews, J. H., and Dewey, L. H., *8th Intern. Congr. Appl. Chem. Sect. IX, Orig. Comm.*, **20**, 247 (1912). For data on the absorption of chromic acid, potassium chromate and dichromate and permanganate solutions, see Viterbi, E., and Krausz, G., *Gazz. chim. ital.*, **57**, 690 (1927); Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 913 (1930); *Chem. Abs.*, **25**, 2053 (1931); Tawde, N. R., *J. Indian Chem. Soc.*, **8**, 499 (1931); *Chem. Abs.*, **26**, 395 (1932); Rao, A. L. S., *Current Sci.*, **6**, 154 (1937); *Brit. Chem. Abs.*, **A1**, 59 (1938); *Proc. Indian Acad. Sci.*, **6A**, 293 (1937).

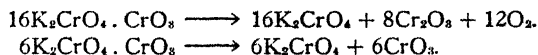
²¹⁵ Plotnikow, J., *Bull. acad. sci. Russ.*, 1093 (1919); *Chem. Abs.*, **17**, 2231 (1923).

²¹⁶ Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, **169**, 381 (1928); see also Wulff, P., and Ammann, H., *Compt. rend. IX, Congr. int. Phot. Sci. appl.*, 10 pp., 1935; *Brit. Chem. Abs.*, **A1**, 90, 1938; Ammann-Brass, H., *Z. wiss. Phot.*, **36**, 33 (1937); *Brit. Chem. Abs.*, **A**, 255, 1937. For the use of a formic acid-formate buffer in the photoreduction, see Wulff, P., and Ammann, H., *Compt. rend. IX, Congr. int. Phot. Sci. appl.*, 1935; *Chem. Abs.*, **31**, 8381 (1937).

²¹⁷ Forbes, G. S., and Leighton, P. A., *J. Phys. Chem.*, **30**, 1628 (1926).

Morton²¹⁸ finds that, under suitable conditions, as in the presence of ethyl alcohol, dichromate solutions are affected by light absorbed by the dichromate. With increasing acidity, the oxidizing power of the dichromate solutions in darkness increases so that the apparent action of light decreases.

Reactions between potassium dichromate and gelatin under the influence of light have been studied and have been applied in photography. The photochemical mechanism is not yet understood, and no attempt will be made to review the early work on the nature of the reaction. According to Plotnikow and Karschulin,²¹⁹ the reaction begins at 5950Å, reaches a maximum at 5000Å and then decreases to about 2400Å, at least in the case of films sensitized with potassium dichromate and cresyl blue, 2BS. On the other hand, Eder²²⁰ found the action of light on chromated gelatin to begin at 550m μ , to reach a maximum between 470 and 430m μ , and to become very slight beyond 380m μ .²²¹ Popovitzkii²²² states that from earlier work of Eder, it is known that gelatin so transformed represents a compound with chromium salts, no organic oxidation products entering the composition. Popovitzkii suggested the formula $4\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}$, for the chromium complex, which agreed better with the analytical results than the formulas $\text{Cr}_2\text{O}_3 \cdot 2\text{CrO}_3$ or $\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}_3$ suggested by Eder and Lumière Brothers and Seyewetz. In order to employ the Werner coordination number of six for chromium compounds, the formula given above should be doubled. Two photochemical reactions might be written to account for its formation:



It is presumed that the gelatin having absorbed but not combined with the liberated oxygen can enter into combination with the 8 Cr_2O_3 and 6 CrO_3 with greater ease. Galinsky²²³ suggests that the change resembles a protein denaturation, although no change in the Hausmann numbers or in the digestibility was detected.

The decomposition of chromyl chloride by light into CrO_2 and chlorine, from the nature of the absorption spectrum, requires wave-lengths shorter than 4200Å.²²⁴

Tin Compounds. The molecular absorption coefficient of a solution containing 32.7 gm. stannous chloride per liter and 0.811N in hydrochloric acid corresponds to complete absorption for wave-lengths shorter than 2850Å, partial absorption from 3020 to 3340Å and complete transmission of wave-lengths longer than 3650Å. Stannous chloride solutions do not follow Beer's law, probably because of the formation of such absorbing complexes as HSnCl_3 and H_2SnCl_4 in the presence of increasing amounts of acid. Quantum yield determinations indicate the photochemical oxidation of such solutions to be a chain reaction. Both the photochemical and the thermal reactions are similarly affected by accelerators and inhibitors so that the same chain mechanism probably applies to both.²²⁵

In benzene solutions, the absorption spectra of stannic iodide exhibit maxima which indicate a dissociation yielding an unexcited iodine atom at 3650Å and an

²¹⁸ Morton, D. S., *J. Phys. Chem.*, **33**, 1135 (1929).

²¹⁹ Plotnikow, J., and Karschulin, M., *Z. Physik*, **26**, 277 (1926).

²²⁰ Eder, J. M., *Z. Physik*, **37**, 235 (1926).

²²¹ For a general discussion, see Schömmmer, F., *Phot. Rundschau*, **63**, 120, 138 (1926); Elöd, E., and Berczeli, H., *Kolloid-Z.*, **74**, 305 (1936).

²²² Popovitzkii, A., *J. Russ. Phys. Chem. Soc.*, **55**, 1 (1924); *Chem. Abs.*, **19**, 1664 (1925).

²²³ Galinsky, A., *Biochem. J.*, **24**, 1706 (1930).

²²⁴ Kantzer, M., *Bull. soc. franc. phot.*, **20**, 167 (1933); *Chem. Abs.*, **28**, 4982 (1934); *Compt. rend.*, **196**, 1882; **198**, 1226 (1934); **201**, 1030 (1935).

²²⁵ Haring, R. C., and Walton, J. H., *J. Phys. Chem.*, **37**, 375 (1933).

excited one at 2850Å. In ethyl alcohol, the latter dissociation occurs at 2950Å. In methyl alcohol, no maxima are evident.²²⁶

Certain stannic acids produced either as a result of changes occurring in gelatinous orthostannic acid or formed by the action of nitric acid on tin, acquire a blue coloration on exposure to the ultraviolet rays of sunlight in the presence of certain organic reducing agents, as tartaric, citric and oxalic acids or ethanol. This action is irreversible and is accompanied by decomposition of the reducing agent without visible evolution of gas. The blue color is stable and permanent in the absence of air. The latter destroys the color. Under the same conditions, orthostannic acid does not give the coloration.²²⁷

According to Harada,²²⁸ the formation of the substance $((\text{CH}_3)_3\text{Sn})_2\text{O} \cdot (\text{CH}_3)_3\text{SnI} \cdot \text{H}_2\text{O}$, by the action of sunlight on tin trimethyl iodide (trimethyliodostannane), does not take place unless tin tetramethyl is present.

Mercury and Its Compounds. About 1924-5, Miethe²²⁹ and Stammreich²³⁰ claimed to effect the transformation of mercury into gold by the use of a new type of mercury vapor arc with very high energy input. Nagaoka, of Tokyo,²³¹ independently made similar claims, which for a time were accepted by Haber. Miethe believed he had obtained one part of gold from 100,000,000 parts of mercury, and Nagaoka, by passing high tension sparks between pure tungsten points and mercury under paraffin, claimed to have increased the yield ten thousand times. A sample of gold prepared by the latter is said to have been placed in the American Museum of Natural History.²³² Hönigschmid and Zintl²³³ reported Miethe's material to have an atomic weight of 197.26. The claims called forth a number of papers,²³⁴ some of which contained further confirmatory claims and others of which speculated as to the nature of the intranuclear transformations. The Siemens Works attempted the bombardment of mercury surfaces by electrons in high vacuum, and even patented certain processes for effecting the transformation.²³⁵

Doubts were soon raised on many sides. Tiede, Schleede and Goldschmidt,²³⁶ found that mercury purified by two vacuum distillations was free of gold and gave no gold by Miethe's process and Aston²³⁷ rejected the claims on theoretical grounds. Many workers subsequently reported failures in attempts to duplicate these experiments.²³⁸ Further discussion of reported transmutations of metals by ultraviolet radiations is unnecessary, since the energies required are greater than are available from the usual sources of ultraviolet.

Ether solutions of mercuric chloride (10 gm.) after exposure to sunlight in sealed bottles for a period of five months formed 3.2 gm. of calomel containing an organic substance; the ether contained hydrogen chloride, aldehydes and chlori-

²²⁶ Grant, M., *Trans. Faraday Soc.*, **31**, 433 (1935).

²²⁷ Billen, F., *Ingenieur chimiste*, **9**, 60 (1925); *Chem. Abs.*, **21**, 1933 (1927).

²²⁸ Harada, T., *Bull. Chem. Soc. Japan*, **2**, 105 (1927).

²²⁹ Miethe, A., *Naturwiss.*, **12**, 597 (1924); *Chem. Abs.*, **18**, 3139 (1924); *Naturwiss.*, **13**, 635 (1925)

²³⁰ Stammreich, H., *Z. anorg. allgem. Chem.*, **148**, 93 (1925); **150**, 350, **158**, 185 (1926).

²³¹ Nagaoka, H., *Ind. Eng. Chem., News Ed.*, **3**, 1 (1925); *Naturwiss.*, **13**, 682 (1925)

²³² *Science*, **62**, 1617 (1925).

²³³ Hönigschmid, O., and Zintl, E., *Naturwiss.*, **13**, 644 (1925).

²³⁴ Retschinsky, T., *Physik. Z.*, **26**, 280 (1925); Bernhardt, F., *Physik. Z.*, **27**, 713 (1926); Gascher, A., *Z. Elektrochem.*, **32**, 186 (1926); Kaul, L., *Metalibörse*, **14**, 1432; von Antropoff, A., *Z. angew. Chem.*, **37**, 827 (1924).

²³⁵ French P. 598,140 (1925), to Siemens-Weirke A.-G.; British P. 243,670, 1925, 247,508, 1925, and 248,318, 1925.

²³⁶ Tiede, E., Schleede, A., and Goldschmidt, F., *Ber.*, **59**, 1629 (1926); Riesenfeld, E., and Haase, W., *Ber.*, **58**, 2828 (1925); Miethe, A., and Stammreich, H., *Ber.*, **59B**, 359 (1926).

²³⁷ Aston, F. W., *Nature*, Dec. 19, 1925; Riesenfeld, E., and Haase, W., *Ber.*, **59**, 1625 (1926).

²³⁸ Piutti, A., and Boggio-Lera, E., *Giorn. chim. ind. applicata*, **8**, 59 (1925); Garrett, M. W., *Nature*, **118**, 84 (1926); *Proc. Roy. Soc.*, **112A**, 391 (1926); Shelton, H., and Estey, R., *Phys. Rev.*, **27**, 515 (1926); *J. Frank. Inst.*, July 22, 1926; Harkins, W. D., *Science*, **63**, 1636 (1926); Duhme, E., and Lotz, A., *Ber.*, **59**, 1649 (1926); Haber, F., Jaenicke, J., and Matthias, F., *Ber.*, **59**, 1641 (1926); *Z. anorg. Chem.*, **153**, 153 (1926); Wolfers, F., *J. chim. phys.*, **24**, 727 (1927).

nated compounds.²⁸⁹ Pougnet²⁴⁰ exposed a solution of mercuric chloride in a quartz tube to a mercury vapor lamp. He found that the tube became cloudy almost immediately because of the formation of calomel. After thirty minutes, 42 per cent had been decomposed and the calomel began to darken. After seventy minutes, when the decomposition reached 48 per cent, the reaction ceased, indicating the reaction to be reversible.

In solutions of mercuric chloride of relatively low concentration the photochemical reduction by ferrous chloride goes at a rate nearly independent of the concentration of the ferrous salt.²⁴¹ For a given concentration of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum rate appears to be attained when the salts are present in equimolar quantities (3 molar). Under these conditions, oxygen does not affect the reaction, but when there is a large excess of ferrous chloride, it reduces the quantity of calomel obtainable. The most effective wave-lengths appeared to be shorter than 2650Å.

When an alcoholic solution of hydrogen sulfide is gradually added to mercury halides in suspension or in solution, complex compounds of the general formula $\text{HgX}_2 \cdot 2\text{HgS}$ result. These compounds, of various shades of red and yellow, readily undergo a color change in direct or diffuse daylight, regaining their original colors in darkness.²⁴²

Mercuric iodide, in solutions less than 1.5 molar in potassium hydroxide, is converted into the unstable dark red $\text{HgI}_2 \cdot \text{HgO}$, which decomposes into mercuric oxide, but is unaffected by light.²⁴³ In more alkaline solutions (2-6 molar), there is formed a white complex, $3\text{HgI}_2 \cdot \text{HgO} \cdot 3\text{KOH}$, which is decomposed into HgO by light. In solutions stronger in alkali than 7 molar, there is formed a white complex, $\text{HgI}_2 \cdot 2(\text{or } 3)\text{HgO} \cdot \text{XKOH}$ which, when dried, is slowly decomposed by light.

Lüppo-Cramer²⁴⁴ finds that red mercuric iodide present with gum arabic in a gelatin film is light- and color-sensitive, forming a developable latent image.

Cinnabar is blackened by ultraviolet light,²⁴⁵ but the nature of the reaction has not yet been explained. Cropp²⁴⁶ attributed it to a decomposition into the elements.

Mercurous sulfate also darkens rapidly and independently of the presence of air. Skinner²⁴⁷ does not believe there to be production of mercury and mercuric salt and suggests that a dark subsalt or a polymeric modification may be formed.

Halogen mercury thiocyanates are phototropic, and complex halides of mercury such as HgI_2Br , HgI_2Cl and HgBrCl , are somewhat less so.²⁴⁸

Cobalt and Nickel. The differences in color of aqueous cobalt salts under

²⁸⁹ Puxeddu, E., *Gazz. chim. ital.*, **59**, 160 (1929).

²⁴⁰ Pougnet, J., *Compt. rend.*, **161**, 348 (1915); *J. Soc. Chem. Ind.*, **34**, 1053 (1915).

²⁴¹ Winther, C., *Z. wiss. Phot.*, **11**, 60 (1912); *Chem. Abs.*, **6**, 2042 (1912).

²⁴² Varalalu, T., Ram, A., and Rao, B., *J. Sci. Assoc. Maharajah's College, Visianagaram*, **1**, 107 (1924); *Chem. Abs.*, **18**, 3529 (1924).

²⁴³ Montigne, E., *Bull. soc. Chim.*, **2**, 290 (1935); *Brit. Chem. Abs.*, **A**, 458 (1935).

²⁴⁴ Lüppo-Cramer, *Phot. Korrr.*, **65**, 97 (1929); *Chem. Abs.*, **25**, 885 (1931).

²⁴⁵ Brosset, C., *Naturewissenschaften*, **24**, 813 (1936).

²⁴⁶ Cropp, W., *Proc. Austral. Inst. Met.*, No. **52**, 259 (1923).

²⁴⁷ Skinner, S., *Proc. Camb. Phil. Soc.*, **12**, 260 (1904); *J. Chem. Soc.*, **86**, ii, 173 (1904).

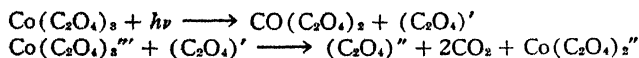
²⁴⁸ For further discussions of phototropy in other complex mercury compounds, see Rao, S. V. R., and Watson, H. E., *J. Phys. Chem.*, **32**, 1354 (1928), and Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929). Slight decomposition is believed to account for the yellow to brown color formed on the irradiation of mercury fulminate by A. Borocco, *Compt. rend.*, **207**, 166 (1938).

various conditions have been the subject of a great number of investigations, but these lie beyond the scope of the present text.²⁴⁹

Baly²⁵⁰ finds that on exposure to daylight in the air, nickel carbonate reversibly darkens in color, due to the production of Ni_2O_3 or nickel hydroxide. Extraction of the blackened material with warm water yielded a small amount of formaldehyde, and on evaporation of the filtrate, it was claimed that there were found the nickel salts of some organic acids and some carbohydrate. Similar results were obtained also, it was claimed, with cobalt carbonate.

Cobalt trinitrotri-amine in acid solution decomposes completely to cobaltous salts both in light and in darkness. In the dark reaction, there are two stages, each being a unimolecular process. The intermediate product is light-sensitive, radiations of 3660A causing decomposition with a quantum yield of 0.37.²⁵¹ On the other hand, the photodecomposition of the cobalt trinitrotri-amine appeared to take place in one stage, the velocity, unlike that of the dark reaction, being independent of the acid concentration. The quantum yield is 0.2 (3660A) and the temperature coefficient 1.03 for the velocity.

On illumination of a solution of racemic $\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3$ by dextro-circularly polarized light (5890A), the cobalt compound becomes levorotatory.²⁵² The decomposition of this compound (0.02-0.002M) by 4360, 4050, 3660 and 3130A is a reaction of zero order, according to Murgulescu,²⁵³ who formulates it



in agreement with Jäger and Berger, but not with Vranek.²⁵⁴

The hydrolysis of aqueous solutions of hexamminecobaltic chloride, nitroamminecobaltic chloride, *cis* and *trans*-dinitrotetrammine cobalt, the two forms of trinitrotri-aminecobalt, and *cis*-tetranitrodiamminecobalt are greatly accelerated by light.²⁵⁵ The cobalt separates, except from dilute solutions in which it remains as sol, as brownish-black cobaltic hydroxide, nitrite ions remaining in the solutions. The photochemical decomposition of all these nitroamminecobalt compounds is an irreversible reaction of the first order in which the wave-length 3660A is most active. Increase in the number of nitro-groups in the nucleus diminishes the photochemical stability; trinitrotri-aminecobalt occupies an intermediate position because of its electrically neutral nucleus. Among stereoisomeric salts, the *trans* compound is the more stable. The velocity of reaction is about one and one-half times as great in acid as in neutral solutions, but is largely independent of the pH. According to Schwarz and Tede,²⁵⁶ the stability of the complex nucleus diminishes with increasing electroaffinity of the coördinately united anion, in the decreasing order, carbonate, oxalate, nitrite, bromide, chloride, sulfate. The inverted position of the oxalate and nitrite ions is attributed to stereo-

²⁴⁹ Mazetti, C., *Gazz. chim. ital.*, **56**, 589, 595 (1926); Hantzsch, A., *Z. anorg. Chem.*, **159**, 273 (1927); Vaillant, P., *Compt. rend.*, **189**, 747 (1929); Brode, W. R., *Proc. Roy. Soc.*, **118A**, 286 (1928); Brode, W. R., and Morton, R. A., *ibid.*, **120A**, 21 (1928); Brdicka, R., *Collection Czechoslov. Chem. Comm.*, **2**, 545 (1930); *Chem. Abs.*, **25**, 467 (1931); Howell, O. R., and Jackson, A., *Proc. Roy. Soc.*, **142A**, 587 (1933); Macwalter, R. J., and Barratt, S., *J. Chem. Soc.*, 517 (1934).

²⁵⁰ Baly, E. C. C., *Phot. J.*, **72**, 474 (1932).

²⁵¹ Luther, R., and Frieser, H., *Z. Elektrochem.*, **36**, 141 (1930).

²⁵² Tsuchida, R., Nakamura, A., and Kobayashi, M., *J. Chem. Soc. Japan*, **56**, 1335 (1935); *Brit. Chem. Abs.*, **A1**, 318 (1937).

²⁵³ Murgulescu, I. G., *Bul. soc. stiinte Cluj*, **8**, 193 (1935); *Chem. Abs.*, **30**, 4402 (1936).

²⁵⁴ Vranek, J., *Z. Elektrochem.*, **23**, 340 (1917).

²⁵⁵ Schwarz, R., and Weiss, H., *Ber.*, **58**, 746 (1925).

²⁵⁶ Schwarz, R., and Tede, K., *Ber.*, **60**, 63 (1927).

chemical factors and probable ring formation in the case of the oxalato-residue. In the cobaltpentammine series, the sequence is carbonate, chloride, oxalate, sulfite, nitrite, nitrate (equal to sulfate). The exceptional position of the chloride ion is due to its non-complex character. The presence of water molecules in the complex increases the tendency to hydrolyze. The complex compounds of chromium are less stable and more subject to photochemical change than are those of cobalt.

Tungsten and Molybdenum. The light-sensitivity of the reduction of tungstic acid by glucose to a blue product was studied by Vasilief-Sinzova.²⁵⁷ The reduction appeared to follow a monomolecular course. The light-sensitivity of freshly prepared solutions of tungstic acid increases with increase of the concentration of added hydrochloric acid up to 0.47 normal, and then decreases, perhaps because the number of molecules of H_2WO_4 sensitive to light increases until the coagulating effect of the acid predominates.

Underlying these observations is the fact that when aqueous solutions of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, polymerization changes occur in the dissolved tungstic acid, hexatungstic acid being first produced. With the addition of more acid there is a further polymerization to metatungstic acid, which is probably a diparatungstic acid, and in the presence of other acids, such as arsenic and phosphoric, heteropolytungstic acids are formed. These changes have been followed by light absorption and diffusion methods.²⁵⁸ Such reactions have been made the basis of a patent for ultraviolet-sensitive layers suitable for actinometric purposes.²⁵⁹ The layer contains compounds of molybdenum, tungsten or thallium, together with an oxidizable substance as glucose, made slightly acid by hydrochloric or citric acids. On exposure to wave-lengths shorter than 4000Å, the layer changes from white to blue.

Hanzawa²⁶⁰ described a chemical actinometer using ammonium molybdate in dilute hydrochloric acid containing small quantities of ethanol. Ghosh and Bhattacharya²⁶¹ find the photochemical reduction of tungstic and molybdic acid sols by alcohol to be of zero order. The velocity constants were found to decrease in sols which had aged, but the velocity constants of the latter could be increased to values greater than those of fresh sols by heating at 70°C. for eight minutes. In the presence of univalent ions the sols are less light sensitive. According to Sachs,²⁶² the best method for the preparation of molybdenum blue is the reduction of a solution of sodium molybdate, acidified with hydrochloric acid, by formic acid in the light of a mercury arc. Hydrogen may also serve as the reducing agent.²⁶³

When exposed to sunlight in a sealed bottle, an ether solution of titanium tetrachloride turned brown during the second day, and ultimately became green. On low temperature evaporation of the solvent, the mixture became violet, suggesting the green and violet modifications of titanium trichloride.

The Rare Earths. Boll²⁶⁴ studied the rate of hydrolysis of tetrachloro-

²⁵⁷ Vasilief-Sinzova, A., *J. Chim. Ukraine*, **1**, 425 (1925); *Chem. Abs.*, **20**, 2792 (1926).

²⁵⁸ Jander, G., Majert, D., and Aden, T., *Z. anorg. Chem.*, **180**, 129 (1929).

²⁵⁹ Sheppard, S. E., and Eberlin, L. W., U. S. P. 1,934,451, Sept. 11, 1933, to Eastman Kodak Co.; *Brit. Chem. Abs.*, **B**, 873 (1934).

²⁶⁰ Hanzawa, T., *J. Agr. Chem. Soc. Japan*, **6**, 1093 (1930); *Chem. Abs.*, **25**, 2643 (1931).

²⁶¹ Ghosh, S., and Bhattacharya, A. K., *J. Indian Chem. Soc.*, **7**, 717 (1930); *Chem. Abs.*, **25**, 252 (1931); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 29 (1932); *Chem. Abs.*, **27**, 2097 (1933).

²⁶² Sachs, D., *J. chim. phys.*, **29**, 474 (1932).

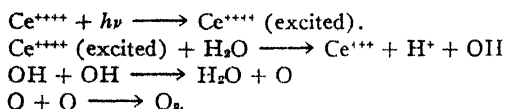
²⁶³ Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930).

²⁶⁴ Boll, M., *Compt. rend.*, **156**, 138 (1914); *J. Chem. Soc.*, **104**, ii, 171 (1913). For data on various platinum complexes, see Lifschitz, I., and Frenctjes, W., *Z. anorg. allgem. Chem.*, **233**, 1 (1937).

platinic acid when submitted to radiations of different energy, the amount of radiation reaching the solution being controlled by a cell containing a dilute solution of caffeine, the concentration and thickness of the caffeine layer being varied. A later study by Boll²⁶⁵ of the reaction in very dilute aqueous solution shows the progress of the photochemical reaction by measuring the increase in the electrical conductivity of the solution.

By the action of hydrogen and short ultraviolet rays, Krauss and Bruchhaus²⁶⁶ reduced a brown solution made by dissolving ruthenium hydroxide in hydrochloric acid to a bright, transparent, orange-colored solution, containing bivalent ruthenium. Colorless liquid ruthenium pentacarbonyl in light evolves carbon monoxide and produces orange-red, pseudo-hexagonal plates of $\text{Ru}_2(\text{CO})_9$. The latter, when dissolved in glacial acetic acid become lilac in sunlight.²⁶⁷

Ultraviolet light causes the liberation of oxygen from a 0.1 molar solution of ceric perchlorate in molar perchloric acid. The quantum efficiency is at first about 0.1. Since the perchlorate ion is not decomposed, the following mechanism was suggested by Weiss and Porret.²⁶⁸



The accumulation of Ce^{+++} retards the reaction, probably by the loss of an electron to the OH molecule with formation of Ce^{++++} and the hydroxyl ion.

Uranium Compounds. Uranium is the only element other than the rare earths, whose compounds exhibit line absorption spectra.²⁶⁹

An acid mixture of solutions of sodium hypophosphite and uranyl sulfate remains unchanged in darkness, but when exposed to light, rapidly deposits a green colloidal precipitate containing 54.5-56 per cent of uranium and 15.75-17.5 per cent of phosphorus, and consisting of hypophosphite with some phosphite and phosphate, mixed with sodium phosphate and uranous sulfate.²⁷⁰

Frequent examples of the use of uranyl salts as photosensitizers will be found in other chapters, particularly in connection with the photochemical behavior of the organic acids. Rousseau²⁷¹ subjected salts or solutions of salts of uranium, manganese, iron or nickel to the action of solar or ultraviolet radiation, and then added the irradiated salts to liquids in which photocatalysis or the sterilization or activation of ferments is to be effected.

Zinc oxide has also been widely employed as a photosensitizer. Winther²⁷² found that when certain samples of zinc oxide were strongly illuminated, in the presence of air, by light filtered through ordinary glass, a substance appeared in

²⁶⁵ Boll, M., *Ann. Phys.*, **2**, 54, 266 (1914); *J. Chem. Soc.*, **108**, ii, 123 (1915).

²⁶⁶ Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem.*, **189**, 53 (1930).

²⁶⁷ Manchot, W., and Manchot, W. J., *Z. anorg. allgem. Chem.*, **226**, 385 (1936).

²⁶⁸ Weiss, J., and Porret, D., *Nature*, **139**, 1019 (1937).

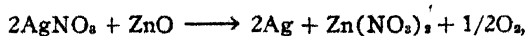
²⁶⁹ Details of the absorption and fluorescence spectra of uranium compounds are given by van Heel, A., *Comm. Phys. Lab. Univ. Leiden, Suppl. No. 55B to Nos. 169-180* (1925); *Chem. Abs.*, **21**, 3311 (1927); Ephraïm, F., and Mezener, M., *Helv. Chim. Acta*, **16**, 1257 (1933); Ghosh, J. C., and Mitra, B. N., *Quart. J. Indian Chem. Soc.*, **4**, 353 (1928); Levshin, V. L., *Bull. acad. sci., U.R.S.S., Classe sci. math. nat., Ser. Phys.*, **No. 2**, 185 (1937); *Chem. Abs.*, **31**, 8380 (1937). For the photochemical liberation of iodine from potassium iodide by uranyl sulfate solutions, see Montignie, E., *Bull. soc. chim.*, **5**, 564 (1938).

²⁷⁰ Dienert, F., and Villemaine, F., *Compt. rend.*, **199**, 1113 (1934). See also Chretien, A., and Kraft, J., *Compt. rend.*, **204**, 1736 (1937).

²⁷¹ Rousseau, E., *British P.* 226,534, Dec. 13, 1924; *Brit. Chem. Abs.*, **B**, 406 (1926).

²⁷² Winther, C., *Z. wiss. Phot.*, **21**, 168 (1921).

the gas phase which was capable of oxidizing iodide ion to iodine. In the use of this zinc compound for photosensitization of the decomposition of silver salts to sunlight



Perret²⁷³ found silver peroxide to be formed as an intermediary product. In the reduction of mercuric chloride to calomel by zinc oxide in sunlight, four to fifteen days were required for a notable transformation; the reaction attained a stationary state. When the reaction is of zero order, it is greatly accelerated by dextrose and by sucrose. In the presence of air, the sensitizing action of zinc oxide on the photolysis of calomel consists in the simultaneous oxidation and reduction of the salt. Bhattacharya and Dhar²⁷⁴ listed twenty-nine reactions sensitized by zinc oxide, including among others, the separation of gold from its chloride, the oxidation of potassium iodide by potassium persulfate, oxidation of sodium nitrite by iodine, oxidation of hydroxylamine or of hydrazine by iodine, decomposition of mercuric oxide, and decomposition of aqueous solutions of potassium permanganate or of potassium persulfate.

To account for the inactivity of many samples of zinc oxide, Jung and Kunau²⁷⁵ studied samples prepared by various methods. Only those obtained by roasting the nitrate proved to be active which suggested that a zinc oxynitrate rather than the oxide might be the true photosensitizing agent. McMorris and Dickinson²⁷⁶ identified nitrogen dioxide as the gaseous product formed in small quantity when zinc oxide (prepared from the nitrate) is strongly illuminated, in a stream of oxygen, by the mercury arc radiations filtered through water and Pyrex glass. Baur²⁷⁷ held that on the absorption of energy, zinc oxide is converted into a "phototrope," one-half of which is capable of oxidizing a neighboring substance, while the other half reduces the same substance. Such a conception of intramolecular electrolysis is however, unnecessary for the explanation of photosensitization by zinc oxide, since it has been found that a gaseous oxidizing agent is liberated from zinc oxide on irradiation.

²⁷³ Perret, A., *J. chim. phys.*, **23**, 97 (1926).

²⁷⁴ Bhattacharya, A. K., and Dhar, N. R., *Quart. J. Indian Chem. Soc.*, **4**, 299 (1927), *Chem. Abs.*, **22**, 915 (1928).

²⁷⁵ Jung, G., and Kunau, E., *Z. physik. Chem.*, **15B**, 45 (1931).

²⁷⁶ McMorris, J., and Dickinson, R. G., *J. Am. Chem. Soc.*, **54**, 4248 (1932).

²⁷⁷ Baur, E., *Trans. Faraday Soc.*, **21**, 627 (1925), see also Chapter 16.

Chapter 21

Photochemical Reactions of Inorganic Solids

The present theories of photoprocesses in crystals have resulted from attempts to interpret the experimental studies of the effects of the absorption of light by ionic alkali halide crystals by the methods of quantum mechanics recently developed for the study of the properties of metals.¹ In large part, the experimental foundation has been laid at Göttingen, as an extension of the studies of Gudden and Pohl² on the photoconductivity of certain homopolar crystal lattices, notably the diamond. After a number of attempts had been made to obtain similar measurements upon variously colored rock salt crystals,³ a thorough study was undertaken of the formation by ultraviolet light of a yellow color in alkali halides. This phenomenon had been observed by Goldstein⁴ as early as 1896. To obtain an understanding of the nature of this process, Hilsch and Pohl⁵ made observations of the far ultraviolet (including the Schumann region) absorption spectra of a number of alkali halides. In some cases, the halides were deposited upon quartz plates by vacuum sublimation. It was found that the nature of the absorption was determined primarily by the halogen ions, and was relatively but little influenced by the nature of the cation. The extinction curves showed definite sharp maxima. Absorption in these bands was believed to effect a transfer of an electron from a halogen ion of the crystal lattice to an adjacent metal cation, producing free halogen and metal atoms. In each case, the band of longest wave-length (corresponding to the absorption of the smallest effective quantum) was attributed to the liberation of the atoms in their normal states. The energy required for this was at first held to be equal to, first, that required to separate an electron from a halogen ion (its electron affinity E) and, second, that required to overcome the coulombic attraction between the sodium and halogen ions (the coulombic part of the lattice energy of the crystal Q). This energy requirement would be diminished by the work necessary to ionize the alkali atom (its ionization potential I), since this energy is liberated when the ion is converted into the atom. From available data, the values of $Q+E-I$ were calculated for the various halides studied. The correspondence between the calculated energy values and the energy corresponding to the first absorption maxima was only fairly satisfactory. The value calculated for the mean of the lithium, sodium, potassium and caesium iodides was 5.76 electron-volts and the observed value was 5.56 electron-volts.^{6, 7}

¹ Bloch, F., *Z. Physik*, **52**, 555 (1928); **59**, 208 (1930); Wilson, A. H., *Proc. Roy. Soc. London*, **133A**, 458 (1931); **134A**, 277 (1931); Peierls, R., *Ann. Physik*, **4**, 121 (1930).

² Gudden, B., and Pohl, R., *Z. Physik*, **16**, 170 (1923); **17**, 331 (1923).

³ Gyulai, Z., *Z. Physik*, **32**, 103 (1925); **35**, 411 (1926); Flechsig, W., *Ibid*, **46**, 788 (1928).

⁴ Goldstein, E., *Z. Instrdke*, **16**, 211 (1896).

⁵ Hilsch, R., and Pohl, R. W., *Z. Physik*, **57**, 145 (1929); **59**, 812 (1929); **64**, 606 (1930); **68**, 721 (1931). For earlier observations, see Pfund, A. H., *Phys. Rev.*, **32**, 39 (1928) and for other halides, Ottmer, R., *Z. Physik*, **46**, 798 (1928).

⁶ See also Bonhoeffer, K., and Harteck, P., "Grundlagen der Photochemie," p. 141, Dresden, T. Steinkopff; Sponer, H., "Molekülspektren und Ihre Anwendung auf Chemisch Probleme," II, 339-361, Berlin, J. Springer. de Boer, J. H., "Electron Emission and Adsorption Phenomena," Cambridge Univ. Press, 1935, 239.

The absorption maxima at shorter wave-lengths were attributed to the liberation of the elements in excited states. The difference between the first and second maxima in the spectra of the iodides of alkalis other than caesium, expressed in volts, was 1.02. That between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the iodine atom is, from atomic spectra, 0.937 volt. In the case of the bromides, the corresponding values were 0.52 volt from the separation of the absorption maxima of the crystals and 0.454 volt from atomic spectra.

The third maximum observed in the iodide spectra was attributed to the production of a normal halogen and an excited alkali atom. The caesium halides are exceptional, since in these the crystal structure is different. Two extra maxima appear in caesium iodide.

The yellow coloration produced by irradiation in the absorption bands of the halides or by the action of x-rays was attributed to the production of alkali metal atoms, the formation of which is analogous to that of the latent image in the case of silver bromide. The yellow color⁸ produced by irradiation of sodium chloride crystals corresponds to an absorption maximum at 4650Å. This induced coloration is but slight and it is said that but few color centers are usually formed. Longer exposures or the use of more intense light sources fail to increase greatly the yield of color centers. The yields of these color centers as determined by absorption measurements give rather definite information regarding the quantum yields of the primary photoprocess. Such information can but rarely be obtained in the study of photochemical processes conducted in gaseous or liquid systems. In crystals at room temperatures, Smakula⁹ found that during irradiation with very low light intensities (few quanta), the yield approached unity. With more intense irradiation, however, a condition of saturation was reached, the quantum yield dropping below unity. Under these conditions, the electron displaced was believed to return to its original location. When low intensities were used, the fewer electrons displaced throughout the crystal were thought to be able to acquire energy from the thermal motion of the crystal lattice. This energy lessened their chances of regaining their initial states.

It soon became evident that this relatively simple picture of the processes occurring in an ionic crystal required modification. The absorption of the induced color centers was observed to differ from that of the same alkali atoms in the vapor phase. It was found to be dependent upon the nature of the lattice in which the atoms were believed to be liberated. Thus, the induced maximum for the sodium salts lies at 3480Å in the fluoride, at 4650Å in the chloride and at 5400Å in the bromide. Mollwo¹⁰ finds the color center frequency to be inversely proportional to the square of the lattice constant. It may be displaced toward longer wave-lengths by an increase of temperature. It has also been found that the formation of appreciable amounts of the latent image or so-called F color centers depends upon the presence of defects in the lattice. The more perfect the crystal, the lower are the yields of the latent image, the electron immediately returning to the halogen atom after it has been displaced by absorption unless the energetic

⁷ Born, M., [*Z. Physik*, **79**, 62 (1932)] raised certain objections to the calculation of the wave-length of the first maximum, but it has been suggested that these may be overcome by taking into account polarization effects in the calculations of the lattice energies. See also, Klemm, W., *Z. Physik*, **82**, 529 (1933); Fues, E., *Ibid.*, **82**, 536 (1933); Mayer, J. E., *J. Chem. Physics*, **1**, 270 (1933).

⁸ This must be distinguished from the blue color of certain samples of rock salt which is due to the presence of colloidal dispersed sodium. Phipps, T. E., and Brude, W. R., *J. Phys. Chem.*, **30**, 507 (1926); Leroux, P., *Compt. rend.*, **188**, 904 (1929).

⁹ Smakula, A., *Z. Physik*, **63**, 762 (1930).

¹⁰ Mollwo, E., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1931**, 97; **1932**, 254; *Chem. Abs.*, **26**, 5847 (1932); **27**, 665 (1933). Fröhlich, H., *Z. Physik*, **80**, 819 (1933).

conditions are modified by the presence of lattice defects, foreign atoms or surface irregularities. Smekal¹¹ has employed the localization of the color centers induced by irradiation as a means of studying the ultramicroscopic crevice imperfections of crystals.

The influence of the lattice structure upon the phenomenon is particularly emphasized in the newer theoretical approach to the problem. This is based upon a consideration of the energy levels of the crystal as a whole rather than of the energy levels of the isolated metal and halogen atoms or ions. The modifications in the potential energy diagrams of the isolated atoms which result when they are made to approach each other to the distances in the crystal lattice are developed mathematically. In this way there may be obtained a model analogous to that which has proved useful in recent work on the structure of metals. Such a model provides a potential energy diagram for an electron moving in the periodic force fields of a lattice.¹² Although the mathematical methods employed in this approach can be comprehended only by specialists, mention may be made of some of the results to which they have led. The sharp energy levels of the individual atoms are, in the crystal, transformed into broad bands or zones, each of which can accommodate the number of electrons required to fill in the corresponding energy level of each of the atoms in the lattice. Within each such continuous zone there are an almost infinite number of energy levels. For this reason, if a zone is only partially filled with the number of electrons which the zone can hold, these electrons are free to move as in a metal. In the alkali halide crystals, ions rather than atoms are present, since the halogen atoms have acquired from the metal atoms their loosely bound valence electrons. This means that the zone corresponding to the 4P level of the halide, *c.g.*, bromine, ions is filled with electrons.¹³ On the other hand, the zone of higher energy level of the metal ions is empty (at 0°K). If by heat or light, electrons could be raised into this zone to partially fill it, these electrons would also be able to move freely throughout the crystal and render it conducting. Between these two zones there is a wide region of forbidden energy levels. In actual rather than ideal crystals, there may be additional energy levels situated just below the upper conducting energy zone. These may be due to the presence of lattice irregularities or to surface effects.

According to current theories, the color centers produced by the action of ultraviolet light or x-rays upon the alkali halide crystals are due to the presence of electrons in these localized energy levels below the conduction zone. Irradiation is believed to raise electrons to these levels from a lower level, *c.g.*, of a halide ion, by a two-stage process. It is first raised to a higher level which may or may not lie within the conducting zone. From this it drops back to the final level somewhat below the upper conducting zone. Electrons in this level are responsible for the absorption exhibited by the "latent image" or F centers. The F color centers can also be produced by directly introducing electrons from a pointed cathode¹⁴ or by heating the crystals in an alkali metal vapor. Since different metal vapors produce the same coloration in a crystal, it appears that it is the

¹¹ Smekal, A., *Physik. Z.*, **33**, 204 (1932); de Boer, J. H., *Rec trav. chim.*, **56**, 301 (1937). See also, Lorenz, H., *Fortschr. Mineral., Krist. Petrog.*, **20**, 290 (1936); Blochinzew, D., *Physik. Z. Sowj.*, **10**, 431 (1936).

¹² Gurney, R. W., *Proc. Roy. Soc. London*, **141A**, 209 (1933); Morse, P. M., *Phys. Rev.*, **35**, 1310 (1930); Brillouin, L., *J. physique*, **1**, 377 (1930); Kronig, R., and Penney, W. G., *Proc. Roy. Soc. London*, **130A**, 499 (1931).

¹³ See, for further discussion, Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936).

¹⁴ Stasiw, O., *Nachr. Ges. Wiss. Göttingen Math.-physik. Klasse*, **1932**, 261; Gurney, R. W., *Proc. Roy. Soc. London*, **141A**, 209 (1933).

electrons rather than, as previously supposed, the neutral atoms which are, in some manner, responsible for the color acquired by the crystals.

Hilsch and Pohl¹⁵ showed that heating a crystal with F centers in hydrogen causes their gradual disappearance. At the same time a new absorption band (U band) in the ultraviolet near the long wave-length edge of the characteristic absorption band appears. The same process can be effected, although very inefficiently, by the absorption of light by the F centers. The U centers can also be produced by passing an electric current from the liquid to the crystals during their formation from the fused halide. The absorption of ultraviolet light by the U centers of the crystal reverses the optical process by which they can be formed from the F centers. As the U centers are destroyed, the F centers reappear in a one-to-one correspondence. The U centers were believed due to electrons in discrete energy levels slightly above the lower filled zone. The energetic relations between the upper conductance zone, the lower filled zone and the discrete levels representing the F and U centers have been summarized in a potential energy diagram by Tartakowsky¹⁶ for the sodium chloride crystal. The filled and conductance zones are separated by 7.7 electron-volts, quanta of this magnitude being required to render pure crystals conducting. The F centers lie 2.65 electron-volts below the upper zone, and the U centers, 1.3 electron-volts above the lower zone.

More recently, Hilsch and Pohl¹⁷ suggest that U centers result from the diffusion of hydrogen into the crystal and that alkali hydride molecules are formed.

A large number of investigations deal with the effects of the absorption of light by the U and F centers in crystals at various temperatures. These are primarily of physical rather than chemical interest, since they are concerned in part with photoelectric phenomena and in part, particularly in the case of crystals with foreign atom impurities, with phenomena of phosphorescence and luminescence.¹⁸ These latter provide a basis for understanding the technically important use of luminescent substances in lighting and television. As such, they lie beyond the scope of this work.¹⁹

Another feature which has emerged from the use of quantum mechanics in the treatment of the absorption of light by crystals is a recognition of the fact that light energy absorbed in one portion of a crystal may be propagated throughout the lattice as an excitation wave. In other words, the excited electron and the hole it has left in the lower band may be conceived as moving about the crystal. This excitation wave may be considered, in terms of the de Broglie wave-theory of matter, as a particle called an "exciton" which moves through the crystal. This term was introduced by Frenkel in a mathematical treatment of the degradation and migration of energy in crystals.²⁰ Franck and Teller²¹ discuss the signifi-

¹⁵ Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1933, 322, 406; *Chem. Abs.*, 29, 3237 (1935); *Z. Physik*, 87, 78 (1933); *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe II*, 1, 209 (1935); *Chem. Abs.*, 30, 4763 (1936).

¹⁶ Tartakowsky, P., *Z. Physik*, 90, 504 (1934); Tartakowsky, P., and Poddubny, W., *Ibid.*, 97, 765 (1935).

¹⁷ Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe II* (N.F.), 2, 139 (1936); *Chem. Abs.*, 31, 7754 (1937); *Trans. Faraday Soc.*, 34, 88 (1938).

¹⁸ Hughes, A. L., *Rev. Mod. Phys.*, 8, 294 (1936). Much of the preceding discussion has been based upon this review.

¹⁹ For reviews, see Pohl, R. W., *Kolloid-Z.*, 71, 257 (1935); *Proc. Phys. Soc. London*, 49, No. 274, 3, 36 (1937); *Abhandl. Ges. Wiss. Göttingen, Math.-physik. Klasse, III*, 18, 71 (1937); Leverenz, H. W., and Seitz, F., *J. Applied Phys.*, 10, 479 (1939); Symposium in *Trans. Faraday Soc.*, 35, 1 (1939).

²⁰ Frenkel, J., *Physik. Z. Sowj.*, 9, 158 (1936); *Phys. Rev.*, 37, 17, 1276 (1931); Peierls, R., *Ann Physik*, 13, 905 (1932).

²¹ Franck, J., and Teller, E., *J. Chem. Phys.*, 6, 861 (1938).

cance of this concept in the treatment of photochemical processes induced at locations of a crystal (surfaces or disturbed lattice points) at a distance from the point at which light absorption occurs.

THE SILVER HALIDES AND THE PHOTOGRAPHIC LATENT IMAGE

Present concepts of the latent image²² are in general analogous to those developed in the treatment of the alkali halides. The importance of the photographic process led to a large amount of early work. It was indeed shown by many²³ prior to the work on the alkali halides that the primary photographic process takes place in a halogen ion rather than in silver. Before considering the recent interpretations, brief reference will be made to some of the earlier observations on the products resulting from the prolonged irradiation of the silver halides. It is interesting to recall that the existence of ultraviolet rays was first made known by the demonstration by Ritter of the ability of invisible radiations beyond the blue end of the solar spectrum to blacken silver chloride. Ritter²⁴ also showed that their effect could be reversed by the action of other invisible rays beyond the red. Since the absorption spectra of the bromide and iodide of silver extend into the visible, most studies have been concerned with the effects of visible light.

For a time it was considered, notably by Becquerel and by Carey-Lea, that the initial product of the action of light (latent image) was some subhalide of silver. By the study of artificial photohalides prepared by mixing and simultaneously coagulating silver and silver halide hydrosols, Luppo-Cramer cast doubt upon this. Many were the attempts to prove or disprove the existence of definite photohalides by direct quantitative measurements of the halogen evolved during prolonged irradiation of silver halides. Richardson²⁵ found 8 per cent of the total halogen to be liberated when 26 gms. of silver chloride under water was exposed to sunlight. Baker,²⁶ however, found only 14 mg. of chlorine to be evolved from 51 gms. of silver chloride after a considerable exposure to light. By the use of a special balance, Volmer²⁷ found silver bromide to lose as much as 40 per cent of its bromine on illumination. Negative results having been recorded by Strömberg²⁸ and by Koch and Schrader,²⁹ a careful reinvestigation was made by Hartung.³⁰ By the use of silver bromide films on silvered vitreous silica supports on a special microbalance, he found a maximum loss of 9% per cent of the total halogen. Similar results were obtained with silver chloride. Studies of the rate of recombination of thin silver films gave no evidence of the formation of silver subbromides. This work definitely favored the hypothesis that the formation of the latent image involves the formation of free silver.

In other attempts to solve this problem, varied techniques as microscopic studies of the effects produced by light,³¹ or the alteration of the silver halide x-ray diagram³² have been employed. The latter method gave indications of the formation of crystalline silver. The influence of various ions adsorbed on silver chloride on the liberation of chlorine by light has been studied by Schwarz and Dieffenbacher.³³ In their experiments,

²² Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936); "Proc. 6th Summer Conference (at Mass. Inst. Technology) on Spectroscopy and Its Applications," p. 157, New York, John Wiley and Sons, 1939; Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London*, **164A**, 151 (1938).

²³ Fajans, K., and Frankenburg, W., *Z. Elektrochem.*, **28**, 499 (1922); Sheppard, S. E., and Trivelli, A. P. H., *J. Phys. Chem.*, **29**, 1568 (1925).

²⁴ Ritter, *Nicolson's J.*, **8**, 214 (1804).

²⁵ Richardson, A., *J. Chem. Soc.*, **59**, 536 (1891).

²⁶ Baker, H. B., *Ibid.*, **61**, 728 (1892).

²⁷ Volmer, *Diss.*, Leipzig, **1910**, 41. Cited by Hartung.

²⁸ Strömberg, R., *Z. wiss. Phot.*, **22**, 165 (1924); *Chem. Abv.*, **17**, 3838 (1923).

²⁹ Koch, P. P., and Schrader, F., *Z. Physik*, **6**, 127 (1921); Koch, P. P., and Kreiss, B., *Ibid.*, **32**, 384 (1925).

³⁰ Hartung, E. J., *J. Chem. Soc.*, **125**, 2108 (1924); **121**, 682 (1922); **127**, 2691 (1925); **1926**, 1349.

³¹ Trivelli, A. P. H., and Sheppard, S. E., *J. Phys. Chem.*, **29**, 1568 (1925).

³² Koch, P. P., and Vogler, H., *Ann. Physik*, **77**, 495 (1925); Trillat, J. J., and Motz, H., *J. Phys. Radium*, **7**, 89 (1936).

³³ Schwarz, R., and Dieffenbacher, K., *Z. anorg. Chem.*, **152**, 91 (1926).

50 mole per cent of a foreign nitrate solution was added to a silver nitrate solution which was then precipitated by an amount of sodium chloride less than sufficient to throw out all of the silver chloride. The acetate, citrate, tartrate, tetraborate and sulfate anions did not affect the rate of photodecomposition, but copper, lead, barium and thallium reduced the decomposition to 33, 32, 68 and 29 per cent, respectively, of that of silver chloride with only silver ions adsorbed.

More recently, attempts have been made to determine quantum yields for the photolysis of silver chloride. For exposures involving total absorption of the 3650Å line, Feldmann and Stern³⁴ found a quantum yield of 0.86. The irradiation was conducted under water and the liberated chlorine determined by titration. Subsequently, they found³⁵ for the 3130Å line a value of unity. The silver chloride used had been precipitated in the presence of sodium nitrite. The latter served to combine with the liberated chlorine and lessened the probability of a reversal of the photolysis. With more compact samples of silver chloride, the quantum yield was, however, only 0.13 in the presence of sodium nitrite and 0.20 in its absence. For precipitated silver bromide with sodium nitrite, the 3650 and 4360Å lines gave yields of unity, but for silver bromide precipitated in the absence of sodium nitrite and for crystallized silver bromide in the presence of a nitrite, the yield was only 0.4. Rather similar or lower values had been reported previously by others.³⁶

The yield may be affected not only by the compactness of the material, which alters the probability of the reverse reaction, but also in long continued experiments by absorption of some of the light by liberated silver atoms. MacMahon and Chatterji³⁷ measured the absorption of oxygen by irradiated silver bromide and chloride in a tube containing gold as halogen acceptor. The oxygen is absorbed by the dispersed silver resulting from the photolysis.

During the formation of the latent image, the silver halides exhibit photoconductivity. The absorption band of silver bromide in the visible has a minimum energetic separation from the unfilled upper conductance band of the order of three electron-volts. Electrons raised into this band give rise to conductance.^{37a} An approximate agreement between the sensitivity curves for photoconductance and for the photographic effects was observed by Arrhenius,³⁸ indicating according to present conceptions, that the liberation of an electron by light absorption may be concerned also with the formation of the latent image. Some discrepancies between the curves were noted by Coblenz,³⁹ but Toy⁴⁰ and co-workers explain these as due to the fact that the photoconductance experiments were made on large pure silver bromide crystals and the photographic ones on fine crystals in gelatin. Sheppard and Vanselow⁴¹ calculated that the photoelectrons have in the lattice a mean free path of the order of 10^{-6} cm.

³⁴ Feldmann, P., and Stern, A., *Naturwiss.*, **16**, 539 (1928); *Z. physik. Chem.*, **12B**, 449, 467 (1931).

³⁵ *Z. physik. Chem.*, **26B**, 45 (1934). See, however, Plotnikow, I., *Phot. Korr.*, **67**, 199 (1931), *Chem. Abstr.*, **26**, 1861 (1932).

³⁶ Eggert, J., and Noddack, W., *Z. Physik*, **31**, 922, 942 (1925); Eggert, J., *Z. Elektrochem.*, **32**, 491 (1926).

³⁷ MacMahon, P. S., and Chatterji, A. C., *Proc. 15th Indian Sci. Congr.*, **1928**, 138, *Chem. Abs.*, **25**, 2922 (1931).

^{37a} For a quantum-mechanical treatment of conductance, see Fowler, R. H., *Proc. Roy. Soc. London*, **140A**, 505 (1933); **141A**, 56 (1933).

³⁸ Arrhenius, S., *Sitzb. Akad. Wiss. Wien*, **96**, 831 (1887); Scholl, H., *Ann. Physik*, **16**, 193, 417 (1905); Wilson, W., *Ibid.*, **23**, 107 (1907).

³⁹ Coblenz, W. W., *Bur. Standards Bull.*, **18**, 489 (1922). This section is based in part upon a review by Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936).

⁴⁰ Toy, F. C., *Nature*, **120**, 441 (1922); *Proc. 7th Intern. Congr. Phot.*, **14** (1928); Toy, F. C., and Harrison, G. B., *Nature*, **123**, 679 (1929); *Proc. Roy. Soc. London*, **127A**, 613, 629 (1930).

⁴¹ Sheppard, S. E., and Vanselow, W., *J. Phys. Chem.*, **33**, 250 (1929); Sheppard, S. E., *Phot. J.*, **60**, 397 (1928).

As in the case of the alkali halide crystals, the formation of the latent image may be demonstrated optically. The absorption spectrum of silver bromide extends from about 4700Å to the shorter wave-lengths and exhibits a maximum at about 2200Å. It differs from the spectra of the alkali halides in lacking sharp maxima and minima, although there are indications of their existence. The latent image formed by exposures to the low intensities ordinarily used in photography is not visible, but Hilsch and Pohl⁴² showed that by the use of thicker crystals and greater exposures it could be detected as an induced band in the infrared with a maximum at 6900Å. The absorption spectra of the original crystal and that of the latent image may partially overlap and that of the latent image may tend to become complex as compared with those encountered in the alkali halides. This may be ascribed to a tendency for the liberated silver atoms to become coagulated.⁴³ Hilsch and Pohl calculated from dispersion theory and the observed absorption of the latent image that in both the photographic plate and in irradiated alkali halide crystals, the latent image is due to a concentration of but one color center in 10^6 to 10^7 salt molecules. The quantum yield amounts to about 0.33 to 0.4 color centers per photon under the usual exposure conditions. Blair and Leighton⁴⁴ have given an equation expressing the rate of formation of the latent image.

It has been assumed recently that the latent image corresponds in a general way to the F centers of the alkali halides. According to this view the latent image would represent electron energy levels rather than silver atoms. The manner in which such electronic excitation levels occasion the liberation and coagulation of silver atoms is as yet speculative.⁴⁵

Theories of Sensitivity. It has been stated that the light-sensitivity of the silver halides does not coincide with their absorption curves, since it has a maximum in the short visible, and drops off in the ultraviolet where the absorption curve is still rising rapidly. A small hump observed by Fesefeld⁴⁶ at about 4300Å in the absorption spectrum of silver iodide does, however, coincide with the region of maximum sensitivity of that salt. There is also some discrepancy between the long-wave thresholds for absorption and photographic action. In part this may be due to the fact that methods for detecting the formation of a latent image by subsequent development are more sensitive than those for measuring the silver halide light absorption curve. Before the development of the theories discussed in connection with the alkali halides, attempts were made to relate the sensitivity threshold to the energy required to remove electrons from the halogen ions of the normal crystal lattice. Wave-lengths longer than those calculated proved, however, to be effective. Frankenburger and Fajans⁴⁷ suggested that submicroscopic flaws in the crystal lattice might serve to lessen the energy required. Pauling⁴⁸ proposed to calculate the threshold wave-length by deducting from the sum of the electron affinity of the halogen and the coulombic energy of the lattice

⁴² Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1930, No. 2, 176; *Chem. Abs.*, 25, 884 (1931); *Z. Physik*, 64, 606 (1930). For analogous results on silver halide grains, see Kirillow, E. A., *Z. wiss. Phot.*, 26, 235 (1929); *Chem. Abs.*, 23, 1829 (1929); Eggert, J., and Schmidt, R., *Z. Physik*, 48, 541 (1928).

⁴³ See Löhle, F., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1933, 271; *Chem. Abs.*, 28, 973 (1934); Savost'yanova, M. V., and Toporetz, A., *Compt. rend. acad. Sci. (U.R.S.S.)*, 2, 225 (1934); *Chem. Abs.*, 28, 5340 (1934).

⁴⁴ Blair, J. M., and Leighton, P. A., *J. Phys. Chem.*, 36, 1649 (1932); *Phot. Kor. (Suppl.)*, 69, 27 (1933).

⁴⁵ See Berg, W. F., *Trans. Faraday Soc.*, 35, 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London*, 168A, 168 (1938).

⁴⁶ Fesefeld, H., *Z. Physik*, 67, 37 (1931).

⁴⁷ Frankenburger, W., and Fajans, K., *Z. physik. Chem.*, 105, 255, 273 (1923). Pressure may prevent the formation of the latent image according to Poindexter, F. E., *J. Opt. Soc. Am.*, 21, 59 (1931).

⁴⁸ Pauling, L., *Phys. Rev.*, 34, 954 (1929).

a term representing the work done when an electron is brought into the crystal from an infinite distance. He believed this latter quantity a function of the diamagnetism of the crystal. It may be recalled that, in the case of the alkali halides, Hilsch and Pohl had used the ionization potential of the metal as the energy quantity to be deducted. They have also suggested that during the ripening of a photographic emulsion there may be produced centers analogous to the U centers of alkali halide crystals. Electrons in these centers could be lifted to the conduction zone by smaller quanta than those needed by electrons in the lower filled level. It appears likely that continued development of the newer quantum mechanical theories may serve to increase greatly our knowledge of the mechanisms involved.⁴⁹

Mention must also be made of the observation that the sensitivity of a photographic emulsion is related to the presence in the grains of specks of a foreign substance.⁵⁰ Development of an exposed grain is known to start at these specks. These were at one time regarded as silver sulfide, serving the function of forming the anodes of minute photoelectric cells.⁵¹ At present, they are thought to be due to the presence of organic sulfur compounds, derived from the gelatin of the emulsion.⁵²

The more recent theories regard the function of the specks as that of concentrating the silver atoms liberated by the light. It may be that light absorbed at other portions of the grain moves through the grain as an "exciton" toward the disturbing speck.⁵³ A radically different theory, due to Stock,⁵⁴ denies the need for postulating sensitivity specks and regards the latent image as excited silver atoms on blocks of the grain, which is assumed to possess a mosaic structure.

Much effort has been expended in determining the properties which render a latent image developable. Toy and Edgerton⁵⁵ found the relative number of developable centers produced in silver bromide grains by exposure to monochromatic light to be proportional to the number of quanta absorbed by the silver bromide. Weigert⁵⁶ conceives of the latent image as complex micelles of silver halide, water, gelatin and "Ursilber" of increased energy content. This energy, which he believes may represent a summation of many quanta, is supposed to activate the developer molecules.

Trivelli⁵⁷ claims that the larger the specks originally present in an unexposed film, the smaller the amount of silver which needs to be added to it during exposure

⁴⁹ Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London*, **164A**, 151 (1938); Berg, W. F., *Trans. Faraday Soc.*, **35**, 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London*, **168A**, 168 (1938).

⁵⁰ Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E., *J. Frank. Inst.*, **194**, 485 (1922); Sheppard, S. E., and Wightman, E. P., *Ibid.*, **195**, 337 (1923); Sheppard, S. E., Wightman, E. P., and Trivelli, A. P. H., *Ibid.*, **196**, 653, 779 (1923); **198**, 507, 629 (1924); **200**, 335 (1925); Sheppard, S. E., Trivelli, A. P. H., and Loveland, R. P., *Ibid.*, **200**, 51 (1925); Clark, W., *Phot. J.*, **48**, 91 (1924); Toy, F. C., *Phil. Mag.*, **44**, 352 (1922); Sheppard, S. E., and Trivelli, A. P. H., *Phot. Korr.*, **64**, 145, 173, 242, 273 (1928); Svedberg, T., *Z. wiss. Phot.*, **20**, 36 (1920); *Chem. Abs.*, **15**, 2393 (1921); *Phot. J.*, **62**, 183, 186, 310 (1922).

⁵¹ Trivelli, A. P. H., *J. Frank. Inst.*, **204**, 649 (1927); **205**, 111 (1928); *Phot. J.*, **68**, 67 (1928). Contra, Harrison, G. B., *Phot. J.*, **71**, *Sci. Tech. (Suppl.)*, 1 (1931).

⁵² Sheppard, S. E., *Phot. J.*, **49**, 380 (1925); *Nature*, **123**, 979 (1929); "Colloid Symposium Monograph," **3**, 76, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1925; Price, T. S., and Rawling, S. O., *Nature*, **116**, 281 (1925); Price, T. S., *Phot. J.*, **65**, 298 (1925); Silberstein, L., *Phil. Mag.*, **5**, 464 (1928).

⁵³ Compare Hecht, K., *Z. Physik*, **77**, 235 (1932).

⁵⁴ Stock, L. W., *Skrifter Norske Videnskaps-Akad Oslo I, Mat.-natur. Klasse*, No. 10, 1-82 (1938); *Chem. Abs.*, **33**, 2827 (1939).

⁵⁵ Toy, F. C., and Edgerton, H. A., *Phil. Mag.*, **48**, 947 (1924).

⁵⁶ Weigert, F., *Z. wiss. Phot.*, **29**, 191 (1930); **30**, 217 (1931); *Chem. Abs.*, **25**, 1170 (1931); **26**, 3739 (1932); *Phot. Korr.*, **70**, (*Suppl.*), 41 (1934); *Naturwiss.*, **19**, 969 (1931).

⁵⁷ Trivelli, A. P. H., *Nature*, **126**, 760 (1930).

in order to produce a developable latent image. Sheppard⁵⁸ finds that the number of silver atoms produced by exposure and the preexisting nuclei are together too small to support the hypothesis of a minimum critical size for development centers. He believes the state and more particularly the orientation of the silver atoms is a more important determinant of the developability of nuclei than their size.⁵⁹ Reinders and Hamburger,⁶⁰ however, maintain that the smallest developable aggregates consist of three, four or more silver atoms or silver sulfide molecules.

The relation between the silver produced on development to the silver produced in the primary photoprocess is known as the development factor. It decreases with the grain size, being 3×10^8 for a grain mass of 6×10^{-12} and 10^3 for a grain mass of 10^{-16} . This is because the larger the grain, the greater the probability that it will contain a sensitizing nucleus of a certain size. Further details⁶¹ of the theory of the sensitivity of photographic emulsions lie beyond the scope of this work.

HERSCHEL EFFECT

In 1839, Sir John Herschel observed that red light causes a fading of the direct photochemical image produced by illuminating silver chloride. For a considerable time, this was regarded as an effect due to oxidation, but the observations of Leszynski⁶² cast doubt on this, and, according to Trivelli,⁶³ more recent workers regard it as due to a photochemical bleaching of the latent image. Absorption of light by the latent image causes a photoconductivity, which tends to restore the original condition of the lattice by removing an electron from the silver atom and restoring it to the halogen. In the case of the alkali halides, the absorption of light by the latent image has two effects, the predominance of either of which is conditioned primarily by the nature of the crystal and its temperature. Bleaching predominates in the silver halides.⁶⁴ Lüppo-Cramer⁶⁵ has shown that the Herschel effect is not entirely confined to the red end of the spectrum, but may also occur when the intensity is small with yellow, green and even with blue light.

SENSITIZATION

Sensitization to Longer Wave-Lengths. It has been observed that a silver bromide hydrosol containing adsorbed silver ion, in contrast to one with adsorbed bromide ion, shows increased absorption in the yellow and green regions. The absorption curve as a whole is shifted toward the longer wave-lengths by 150 to 200A, and at the same time the spectral sensitivity is shifted toward the longer wave-lengths.⁶⁶ Similar effects are also observed in gelatin emulsions. The thallous ion has a similar effect half as great.⁶⁷ To some extent the latent image

⁵⁸ Sheppard, S. E., *Phot. J.*, **71**, 313 (1931); *Chem. Abs.*, **25**, 5631 (1931).

⁵⁹ See also Arens, H., *Z. wiss. Phot.*, **30**, 49 (1931); Sheppard, S. E., *Ber. 8th Intern. Congr. Phot., Dresden*, 1931, 13; *Chem. Abs.*, **27**, 237 (1933).

⁶⁰ Reinders, W., and Hamburger, L., *Z. wiss. Phot.*, **31**, 32, 265 (1932), *Chem. Abs.*, **26**, 4545 (1932); **27**, 2641 (1933).

⁶¹ Fredenhagen, K., and Wellmann, M., *Z. physik. Chem., Bodenstein Festband*, 135 (1931); James, T. H., *J. Chem. Physics*, **2**, 132 (1934); Blair, J. M., and Hylan, M. C., *J. Opt. Soc. Am.*, **23**, 353 (1933); James T. H. and Coleman, J. J., *J. Chem. Phys.*, **2**, 483 (1934).

⁶² Leszynski, W., *Z. wiss. Phot.*, **24**, 275 (1926); *Chem. Abs.*, **21**, 863 (1927).

⁶³ Trivelli, A. P. H., *J. Frank. Inst.*, **207**, 765 (1929).

⁶⁴ Smakula, A., *Z. Physik*, **59**, 603 (1929).

⁶⁵ Lüppo-Cramer, *Phot. Korr.*, **64**, 108 (1928).

⁶⁶ Fromherz, H., *Z. physik. Chem.*, **1B**, 324 (1928), Fajans, K., Fromherz, H., and Karagunis, G., *Z. Elektrochem.*, **33**, 548 (1927); Fajans, K., and Karagunis, G., *Naturwiss.*, **17**, 274 (1929); Fajans, K., and Steiner, W., *Z. physik. Chem.*, **125**, 275, 307 (1927).

⁶⁷ Fromherz, H., and Karagunis, G., *Z. physik. Chem.*, **1B**, 346 (1928).

itself may also act to sensitize a plate to longer wave-lengths.⁶⁸ These effects, however, are all of relatively little importance in comparison with the sensitizing effects which may be brought about by certain organic dyestuffs. These can be used to alter the natural sensitivity of photographic emulsions so as to render them, either approximately equally sensitive to all of the visible wave-lengths or to extend the range of sensitivity into the infrared or to the shorter ultraviolet regions.

In 1873, Vogel noticed that certain dyes, such as Corallin, which has an absorption band in the yellow-green, sensitized plates to the region which these dyes absorb. The Isochromatic plates of fifty years ago, sensitized with eosin, were the first color-sensitive plates to have been generally used. Many other dyes have since been found more satisfactory. Particularly important are the isocyanine dyes, as ethyl red, carbocyanines, including pinacyanol, and a number of others as kryptocyanine and neocyanine. The use of such dyes has made possible the advances in long-range, haze-penetrating, infrared photography.

The theory underlying the action of these dyes is still somewhat obscure. The range of sensitization and the absorption spectra of the dyes do not coincide as closely as had been at first thought to be the case. It has, however, been suggested that the dyes when adsorbed on the halide grains may have their absorption spectra shifted.⁶⁹ In some instances obscure chain reactions may be set up. Not all dyes sensitize when adsorbed. A common constitutional factor in the effective ones appears to be the existence of either two oxygen or two nitrogen atoms in two states of valency, joined by a chain of conjugated double bonds.⁷⁰

Rabinovich has suggested that in solid systems the energy evolved in the photooxidation of the adsorbed sensitizer by atmospheric oxygen may be utilized in the decomposition of the crystals to which it is adsorbed.

Ultraviolet Plates. Duclaux and Jeantet⁷¹ suggested that a photographic plate may be sensitized to the extreme ultraviolet by the application of a thin coating of oil. Lyman⁷² believes the process does not yield results comparable with the Schumann procedure (Chapter 1), but agrees that its possibilities have not been fully explored. The changes in sensitivity and contrast produced by coating plates of various brands with five different fluorescent oils, in the region of 2200-3800Å have been studied by Harrison⁷³ and by Söderman,⁷⁴ the latter finding only Schumann plates to be satisfactory in the range 50-500Å. A 0.5 per cent solution of vaseline in light petroleum may be employed.⁷⁵ Citric acid and salicylates have also been used.⁷⁶ Eggert and Arens⁷⁷ have added to ordinary

⁶⁸ Eggert, J., and Noddack, W., *Z. Physik*, **31**, 942 (1925). *Synthetic Organic Chemicals*, Eastman Kodak Co., Dec. 1927. For the earlier observations, including those of Becquerel, Lüppo-Cramer and of Fajans, see Mees, C. E. K., *J. Frank Inst.*, **201**, 525 (1926).

⁶⁹ See also Rabinovich, A. J., *Sci. and Phot.*, **6**, 288 (1935); *Chem. Abs.*, **30**, 3343 (1936).

⁷⁰ For further studies of the sensitizing action of erythrosine on colloidal solutions of silver bromide, see Bokinik, Y. I., and Il'ina, Z. A., *Acta Physicochim. U.R.S.S.*, **3**, 383 (1935) *Chem. Abs.*, **30**, 3297 (1936). For the recent development of sensitization theories, Wahl, H., *Chim. et Ind.*, **36**, 16 (1936); Rabinovich, A. J., *Acta Physicochim. U.R.S.S.*, **3**, 368 (1935); *Chem. Abs.*, **30**, 3343 (1936); Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936); Bokinik, Y. A., and Il'ina-Bagdasar'yan, Z. A., *J. Phys. Chem. U.R.S.S.*, **11**, 197 (1938); *Chem. Abs.*, **33**, 3277 (1939); Bagdasar'yan, K. S., *Acta Physicochim. U.R.S.S.*, **9**, 205 (1938), *Chem. Abs.*, **33**, 5759 (1939); Sheppard, S. E., Lambert, R. H., and Walker, R. D., *J. Chem. Phys.*, **7**, 426 (1939).

⁷¹ Duclaux, J., and Jeantet, P., *Science*, **58**, 48 (1923); *J. phys. radium*, **2**, 156 (1921); *Chem. Abs.*, **15**, 2798 (1921).

⁷² Lyman, T., *J. Frank Inst.*, 5560, May, 1926.

⁷³ Harrison, G. R., *J. Opt. Soc. Am.*, **11**, 113 (1925).

⁷⁴ Söderman, M., *Z. Physik*, **67**, 790 (1931).

⁷⁵ Beach, A. C. G., *Nature*, **123**, 166 (1929).

⁷⁶ J. and J. F. Thovet, *Bull. seances soc. franç. phys.*, **1932**, 158; *Chem. Abs.*, **27**, 5662 (1933).

⁷⁷ Eggert, J., and Arens, H., German P. 640,157, Dec. 23, 1936. (To I. G. Farbenindustrie); *Chem. Abs.*, **31**, 2112 (1937).

plates a layer containing a wetting agent and a substance such as fluorene or anthracene which fluoresces in the ultraviolet region. The purpose of the wetting agent, saponin or Turkey-red oil, is to aid in the removal of the fluorescent substance in the development bath. Rathenau⁷⁶ suggests impregnating the plate with a filtering dye which absorbs light of fairly long wave-length and then covering it with a sensitizing oil film which acts on short wave-lengths unabsorbed by the dye. Among the dyes proposed were nitrosodimethylamine, methyl orange, fuchsine. As the sensitizer, Cenco pump oil 11021B could be used.

Details of the sodium salicylate method, including the sensitometry of the plates so treated, have been given by Montagne and Ricard,⁷⁹ Kiu,⁸⁰ and Terrien.⁸¹

Ethyl dihydrocollidinedicarboxylate has been proposed.⁸² Sheppard and Vanselow⁸³ use a silver salt of 1-*p*-sulfophenyl-3-methyl-5-pyrazolone, or related compounds. A number of solutions enumerated by Allen and Franklin⁸⁴ for sensitizing plates to radiations shorter than 2500A are shown in Table 20. The aqueous

Table 20. Substances Used for Ultraviolet Sensitization of Plates.

Chemical Name	Trade Name	Solvent	Approximate Concentration	Remarks
1. 1-naphthylamine-4-sulfonic acid	Naphthionic Acid	Water	2%	Add 4% Na ₂ CO ₃
2. 2-naphthylamin-1-sulfonic acid	Eastman's T386	"	2%	"
3. 2-naphthylamine-6-sulfonic acid	Bronner's Acid	"	2% (sat)	"
4. 2-naphthylamine-6,8-disulfonic acid	Amino G Acid	"	4%	"
5. 2-naphthol-6,8-disulfonic acid	G Acid	"	4%	"
6. α -naphthylamine		Ethyl acetate	2%	Add 4cc. alcoholic solution of white shellac per 100 cc.
7. Fluorene		"	2.5%	"
8. Carbazole		"	2%	"
9. Ethyl carbazole		"	2%	"

solutions are merely applied to the plates for a few seconds, after which the plates are allowed to dry in a vertical position. Just before development, the plates should be rinsed with water. When water-insoluble organic substances are used, these should be removed before development by means of acetone. The same treatment should be used on plates treated with fluorescent oils or Eastman sensitizer.

In a photosensitive layer sensitive to the ultraviolet, Sheppard and Eberlin⁸⁵

⁷⁶ Rathenau, G., *Physica*, **2**, 840 (1935).

⁷⁹ Montagne, R., and Ricard, R., *Compt. rend.*, **202**, 477 (1936).

⁸⁰ Kiu, T., *Compt. rend.*, **201**, 1348 (1935); *Sci. ind. phot.*, **8**, 1 (1937); *Chem. Abs.*, **31**, 2948 (1937).

⁸¹ Terrien, J., *Compt. rend.*, **202**, 211 (1936).

⁸² Burroughs, R. E., U. S. P. 1,880,411, Oct. 4, 1933. (To Eastman Kodak Co.). *Chem. Abs.*, **27**, 675 (1933).

⁸³ Sheppard, S. E., and Vanselow, W., U. S. P. 2,066,582 (To Eastman Kodak Co.), *Chem. Abs.*, **31**, 962 (1937).

⁸⁴ Allen, A. J., and Franklin, R. G., *J. Opt. Soc. Am.*, **22**, 469 (1932).

⁸⁵ Sheppard, S. E., and Eberlin, L. W., U. S. P. 1,934,451, Nov. 7, 1934 (To Eastman Kodak Co.); *Chem. Abs.*, **28**, 426 (1934).

use for application to paper dextrose and an oxygen-containing compound of a metal of the sixth periodic group having an atomic weight between 90 and 200, such as sodium tungstate or molybdate.

Russell Effect. It has long been known that a very great number of substances are capable of affecting a photographic plate in the dark (Russell effect). An exhaustive review of the work in this field has been given by Keenan,⁸⁶ who concludes that, in general, a vapor passes from the active substance to the plate, and that it is of the nature of hydrogen peroxide or an organic peroxide.

THE WEIGERT EFFECT

It was shown by Weigert⁸⁷ that exposure of very thin layers of silver chloride (when sensitized by free silver produced by a previous exposure to ordinary light) to plane polarized light renders the layer color-adapted and dichroic, that is, causes it to exhibit different extinction coefficients in polarized light according to the direction of the plane of polarization. This is a sign of a definite anisotropy in the layer. The optical axis of the photoanisotropic system is always parallel to the plane of the electric vector. After a preliminary exposure to polarized light, the orientation set up determines or orients a subsequent decomposition effected by non-polarized light. This Weigert termed induced photoanisotropy. Zocher and Coper⁸⁸ have obtained the effect by the use of circularly polarized light. Weigert regarded the effect as due to definite alterations in the shape of complex silver micelles. It has, however, been shown by Cameron and Taylor⁸⁹ that the effect can be produced in single crystals of silver chloride previously rendered blue by exposure. Both silver and a silver halide lattice are necessary, but gelatin or other components of photographic emulsions or the gel state are not essential. It is suggested that suitably dimensioned and oriented silver particles can respond to polarized light by ejecting electrons in a definite direction. These reform silver from the silver ions in the lattice, the chlorine being assumed to migrate.

Weigert also observed the phenomenon in the photodecomposition of light-sensitive dyes embedded in gelatin.⁹⁰ In cases in which there is rigidity, either of a crystal lattice or of a gel, photoanisotropy effected by polarized light may persist. In gaseous or liquid systems, in which the photochemical products are rapidly disoriented by collisions, it is evanescent.⁹¹

OTHER SILVER COMPOUNDS

Wave-lengths longer than 2500Å are said not to reduce silver nitrate in pure gelatin, unless there is present 10^{-5} gram mole of potassium chloride or bromide per liter of gelatin. Even eosin or rhodamine-silver nitrate-mannitol mixtures are stable in ultraviolet light if they have previously been subjected to ultrafiltration.⁹²

⁸⁶ Keenan, G. L., *Chem. Rev.*, **3**, 95 (1926).

⁸⁷ Weigert, F., *Verhand. deut. physik. Ges.*, **21**, 479 (1919); summarizing statements in *Naturwiss.*, **9**, 583 (1921); **16**, 613 (1928); **19**, 969 (1931); *Z. physik. Chem.*, **3B**, 377 (1929); **4B**, 239, 258 (1929); **18B**, 73 (1932); see also Nikitine, S., *Compt. rend.*, **204**, 973 (1937); **208**, 513, 643 (1939); Cherdintzev, S., *Acta Physicochim. U.R.S.S.*, **3**, 355 (1935); *Chem. Abs.*, **30**, 2110 (1936); Ungar, G., *Compt. rend.*, **208**, 337 (1939).

⁸⁸ Zocher, H., and Coper, K., *Z. physik. Chem.*, **141**, 217 (1929); **132**, 313 (1928). See also Cotton, A., *Compt. rend.*, **189**, 599 (1929).

⁸⁹ Cameron, A. E., and Taylor, A. M., *J. Opt. Soc. Am.*, **24**, 316 (1934).

⁹⁰ See also Nikitine, S., *Compt. rend.*, **208**, 805 (1939).

⁹¹ Ghosh, J. C., and Banerjee, T., [*Kolloid-Z.*, **86**, 372 (1939)] have recently reviewed extensive experiments on the production of circular dichroism in various inorganic sols by irradiation with circularly polarized light during their formation.

⁹² Boknik, Y. A., *J. Phys. Chem. (U.S.S.R.)*, **11**, 190 (1938); *Chem. Abs.*, **33**, 4130 (1939).

A solution containing starch, silver nitrate and an excess of potassium iodide rapidly becomes blue on exposure to light. Since the reaction is not observed in the presence of an excess of the silver ion, it may be assumed that the iodine liberated is derived from potassium iodide adsorbed on silver iodide, the latter exerting an enormous accelerating influence on the oxidation of the former.⁹³

According to Ishii,⁹⁴ the compound $\text{AgKI} \cdot 2\text{H}_2\text{O}$ exists as asbestos-like crystals which change from peach color to dark purple under sunlight and to dark gray under mercury arc light. Rather similar changes are also observed in the colorless compounds $2\text{AgI} \cdot \text{KI} \cdot 1/2\text{H}_2\text{O}$ and $2\text{AgI} \cdot \text{KI} \cdot 2\text{H}_2\text{O}$. The compound $4\text{AgI} \cdot \text{KI} \cdot 2\text{C}_3\text{H}_6\text{O}$ is not affected by sunlight but changes from colorless to a peach color under the mercury arc. $\text{Ag} \cdot 2\text{KI}$ and $\text{Ag} \cdot 6\text{KI}$ are unaffected by light.

Arens and Eggert⁹⁵ found sensitive gelatin emulsions of silver acetylide, azide or oxalate to be developable under suitable conditions. Each of the three salts is white and absorbs in the same region of the ultraviolet as does silver chloride. After a long exposure of the acetylide, a residue of carbon is found on dissolving away the silver. Nitrogen separates directly from the azide on exposure to light of high intensity, but this does not occur as a result of a correspondingly longer exposure to light of a lower intensity. Possibly in this case hydrogen azide is formed. Contrary to what might be expected from their endothermic nature, the amount of silver which separates directly on exposure of either of these three salts is of the same order of magnitude as that formed from silver chloride.

There are photographic processes which do not employ silver salts. Among these are the bleaching of photosensitive dyes, generally by oxidation, diazo-processes in which after the loss of nitrogen the remaining residue of the diazobody can be coupled to form a dye, alkaline bichromate processes in which there forms a chromic oxide capable of tanning gelatin and certain iron processes.

Gelatin impregnated with ferric chloride gives a white image when exposed under a negative.⁹⁶ Mixtures of tartaric acid and ferric salts with selenious acid or with potassium tellurate are reduced in light with the formation of amorphous selenium or tellurium. Sensitive papers utilizing this behavior have been prepared.⁹⁷ The selenium paper gives a bright red and the tellurium paper a black to brown tone. The development and fixation may be carried out with a dilute solution of hydrochloric acid, with the addition, in the case of the tellurium paper, of stannous chloride to prevent the destruction of the image by the unchanged ferric chloride.

THE BLACKENING OF LITHOPONES

The white pigment lithopone, a mixture of zinc sulfide and barium sulfate, is prone to blacken on exposure to ultraviolet radiations from an arc or in sunlight. Eibner⁹⁸ attributed this to an interaction of metallic impurities with the sulfide pigment. Roches⁹⁹ attached much importance to the presence of chlorides, but

⁹³ Hiller, W., *Z. anorg. Chem.*, **219**, 313 (1934); *Brit. Chem. Abs.*, 1934A, 1183.

⁹⁴ Ishii, S., *Repts. Osaka Imp. Ind. Research Inst. Japan*, **11**, No. 20 (1931); *Chem. Abs.*, **25**, 5362 (1931).

⁹⁵ Arens, H., and Eggert, J., *Phot. Korrr.*, **67**, No. 8, 17 (1931); *Veröffentl. wiss. Zentral-Lab. Phot. Abt. AGFA* **3**, 67 (1933); *Chem. Abs.*, **26**, 1529 (1932); **28**, 3012 (1934); Moskovich, S. M., *J. Phys. Chem. (U.S.S.R.)*, **12**, 460 (1938); *Chem. Abs.*, **33**, 4892 (1939).

⁹⁶ Schommer, F., *Atelier Phot.*, **33**, 91 (1926); *Chem. Abs.*, **21**, 538 (1927).

⁹⁷ Pavolini, T., *Giorn. Chim. Ind. Appl.*, **12**, 72 (1930); *J. Soc. Chem. Ind.*, **1930**, Suppl. 533.

⁹⁸ Eibner, A., *Chem. Ztg.*, **49**, 345, 370 (1925). The darkening of red mercuric sulfide was also discussed.

⁹⁹ Roches, C., *Rev. chim. ind.*, **31**, 109 (1922); *Chem. Abs.*, **16**, 3217 (1922). See also Schleede, A., Herter, M., and Kordatzki, W., *Z. physik. Chem.*, **106**, 386 (1923).

did not find iron, cadmium, cobalt or manganese harmful. Brickwedde¹⁰⁰ believed soluble salts whose sulfides are black to promote the change. The elimination of impurities from the raw materials employed in the manufacture of this pigment has greatly increased its light stability.¹⁰¹ It is, nevertheless, true that even carefully purified Wurtzite, zinc blende and unignited zinc sulfide, in the presence of water, blacken when subjected to ultraviolet rays.¹⁰² In an atmosphere of hydrogen, the decomposition products contain hydrogen, zinc, sulfur, and the zinc and sulfate ions. Electrolytes increase the light-sensitivity. By irradiating a suspension of zinc sulfide in water, Job and Emschwiller¹⁰³ had previously obtained sulfur, zinc and hydrogen.

It was believed by Mass and Kempf¹⁰⁴ that the lattice structure is essential to the blackening and that amorphous freshly precipitated zinc sulfide or zinc sulfide which has been ground in a mortar is insensitive to light. Such samples must be subjected to heat treatment to convert them into phosphors before they will blacken.¹⁰⁵ Only luminescent samples exhibit the phenomenon, possibly because neutral atoms of zinc, cadmium or silver must be present in the interstices of the lattice.¹⁰⁶ Mass and Kempf attributed the change in the zinc sulfide to a process analogous to that which occurs during the exposure of silver bromide; zinc and zinc disulfide were assumed to be formed, the zinc appearing in finely divided form on the surface of the mass. It may be that in the primary process, electrons pass from a sulfide ion on the surface of the crystal lattice and discharge a neighboring zinc ion. Irradiation produces photoconductivity, but there are differences in the spectral sensitivity curves for blackening and for photoconductivity. Gordon, Seitz and Quinlan¹⁰⁷ have speculated regarding the nature of the two-quantum shifts of electronic energy-levels involved. They believe the blackening occurs at the surface as an electrolysis of zinc sulfide in solution in the surface moisture under the electromotive force produced by the optically-formed Zn^+ and S^- ions. The liberation of hydrogen noted by Job and Emschwiller has not yet been interpreted in terms of the newer theories.

Glycerol and other polyatomic alcohols have been believed to protect lithopones.¹⁰⁸ Waterglass is also said to be effective.

It was observed by Mass and Kempf that blackened lithopone brightens in darkness owing to the oxidation of metallic zinc, but remains black if no oxygen is present. The rate of bleaching of darkened lithopone and the photoelectric effect of the latter are similar to the behavior of samples of lithopone upon the surface of which zinc has been distilled.¹⁰⁹

To determine the relative effectiveness of various wave-lengths, Pfund¹¹⁰

¹⁰⁰ Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927).

¹⁰¹ Eihner, A., *Farben Ztg.*, **30**, 2600 (1925); *Chem. Abs.*, **19**, 3601 (1925).

¹⁰² Platz, H., and Schenck, P. W., *Z. angew. Chem.*, **49**, 822 (1936).

¹⁰³ Job, A., and Emschwiller, G., *Compt. rend.*, **177**, 313 (1923); see also Weiser, H. B., and Garrison, A. D., *J. Phys. Chem.*, **31**, 1237 (1927).

¹⁰⁴ Mass, E., and Kempf, R., *Z. angew. Chem.*, **36**, 293 (1923); *J. Chem. Soc.*, **124**, ii, 491 (1923).

¹⁰⁵ See, however, Streck, E., *Ann Physik*, **34**, 96 (1939); **35**, 58 (1939).

¹⁰⁶ Seitz, F., *J. Chem. Phys.*, **6**, 454 (1938); Brusilowskii, A. M., Sigal, F. S., and Kabanova, E. Y., *Lakokhroschnyyu Za*, **1935**, No. 3, 11; *Chem. Abs.*, **31**, 6485 (1937); Brusilowskii, A. M., *Org. Chem. Ind. (U.S.S.R.)*, **5**, 493 (1938); *Chem. Abs.*, **33**, 883 (1939).

¹⁰⁷ Gordon, N. T., Seitz, F., and Quinlan, F., *J. Chem. Phys.*, **7**, 4 (1939); compare Stobbe, H., *Z. wiss. Phot.*, **29**, 209 (1930); *Chem. Abs.*, **25**, 1441 (1931).

¹⁰⁸ Nishizawa, Y., *J. Tokyo Chem. Soc.*, **41**, 1054 (1920); *Chem. Abs.*, **15**, 1407 (1921); see also, British P. 156,971, Nov. 25, 1919; Gardner, H. A., and Holdt, P. C., *Paint Mfrs. Assn. Circ.*, **194**, 174 (1924); *Chem. Abs.*, **18**, 910 (1924).

¹⁰⁹ Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927). See also Goshorn, J. C., and Black, C. K., *Ind. Eng. Chem.*, **21**, 348 (1929).

¹¹⁰ Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 375 (1923).

rubbed a sample in water and covered it with a quartz plate. The specimen was then mounted in the focal plane of a quartz spectrograph, so that the entire spectrum from an iron arc was projected upon the lithopone surface, which, by darkening indicated the spectral regions of greatest effectiveness. Wave-lengths longer than 3200A showed very little darkening. By the use of monochromatic light of constant intensities, it was shown that the sensitivity of lithopone is almost nil in the visible spectrum, and rises to a high value in the ultraviolet near 2900A, remaining practically constant at shorter wave-lengths. All samples of lithopones tested by Pfund showed the same general type of sensitivity curves. These curves were obtained by plotting against the wave-lengths the reciprocals of the time in seconds required to produce a visible darkening by these wave-lengths, the intensity being maintained constant. Brickwedde, employing this method, found very different results, the sensitivity beginning at 3700A and showing a subsidiary maximum at 3130A.

In testing lithopones, Gardner and Holdt¹¹¹ use either an exposure to sunlight, or as an accelerated test, to the rays of a mercury or iron arc. When the mercury arc is used, the pigment is exposed as a dried oil paint film on a palette submerged in a shallow layer of water to reproduce a condition of constant humidity. The test should be carried out on the pigment ground in the vehicle in which it is intended to be used. The acid value of the oil medium used has a marked effect, increasing acid values in a series of alkali-refined linseed and tung oils diminishing but not entirely inhibiting the darkening of the pigment. When employing the rays from an iron arc, the lithopone paste is exposed behind a quartz slide, backed by an ordinary glass slide to retard evaporation. When sunlight is used, ordinary thin microscope slides may be used. The degree of darkening may be evaluated by comparison with standards.

Some reversible darkening in daylight of commercial samples of titanium oxide,¹¹² particularly in those containing iron, has been observed to occur. Vermillion is also light-sensitive.¹¹³

EFFECT OF ULTRAVIOLET RADIATIONS ON COLLOIDAL SYSTEMS

Preparation. Although Schulze¹¹⁴ was unable to effect the conversion of metals into dusts by the action of ultraviolet radiation, Svedberg¹¹⁵ succeeded in preparing colloidal sols of metals by applying an observation of Lenard and Wolf¹¹⁶ that certain substances, especially metals, are disintegrated when exposed to ultraviolet rays. Pieces of metal, the surfaces of which had been carefully freed from oxides, were placed in a shallow dish containing a dispersion medium, and exposed to the rays from a Heraeus quartz mercury arc lamp at a distance of a few centimeters. After a few minutes, colloidal sols were obtained from silver, copper, tin and lead, but platinum, aluminum and cadmium remained practically unaffected. The action was especially marked in the case of lead, which yielded a colloidal sol in ethyl alcohol, and a milky liquid, probably containing lead hydroxide, in water. The nature of the dispersion medium had a great influence on the results with silver and lead. Kimura¹¹⁷ tested the effect of ultraviolet rays on silver, copper

¹¹¹ Gardner, H. A., and Holdt, P. C., *U. S. Paint Mfrs. Circ.*, 194, 174 (1924); *Chem. Abs.*, 18, 910 (1924).

¹¹² Williamson, W. O., *Nature*, 140, 238 (1937); 143, 279 (1939).

¹¹³ Six, G., and Bover, J. R., *Paint Manuf.*, 8, 367 (1938); *Chem. Abs.*, 33, 883 (1939).

¹¹⁴ Schulze, F., *Ber. Physik. Ges.*, 1912, 246; *Chem. Abs.*, 6, 1708 (1912).

¹¹⁵ Svedberg, T., *Ber.*, 42, 4375 (1909); *Z. Chem. Ind. Colloide*, 6, 129, 238 (1910).

¹¹⁶ Lenard and Wolf., *Ann. Phys. Chim.*, 37, 443 (1889).

¹¹⁷ Kimura, M., *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 5, 253 (1913); *Chem. Abs.*, 8, 611 (1914).

and an alloy of cadmium 90 per cent and antimony 10 per cent. In a vacuum, no corrosion took place, in air, there was a very slight corrosion, in oxygen somewhat more and in water strong corrosion under the influence of the rays. Nordenson,¹¹⁸ who continued these experiments, using quantitative methods, ascribed the formation of the colloidal sols by the rays to the formation of hydrogen peroxide. This attacks the metal, yielding an oxide or hydrate which after solution is converted to a metallic colloid by the reducing action of the rays.

Dede and Walther¹¹⁹ obtained yellow to bluish-violet colloidal solutions of arsenic by bubbling purified arsine through water exposed to light of short wavelengths.

Voigt¹²⁰ has stated that pure silver nitrate in very dilute solution does not form a silver hydrosol when exposed to the rays from a quartz lamp except in the presence of a protective colloid such as gum arabic. The wave-length is important, ultraviolet rays being required. The ultramicroscopic particles of the gum act as reducing centers.

Wassiljewa¹²¹ notes that if dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained. This, in the presence of various organic substances such as formaldehyde, sucrose, dextrose or dextrin, undergoes reduction on exposure to light, with the formation of an intensely blue solution. If the undialyzed solution is kept for some time, it is found that the reduction process does not occur when the solution is exposed to light. This may be due to the existence of two forms of colloidal tungstic acid, one of which is photochemically inert and the other sensitive to light. The latter changes spontaneously into the former. The reverse transformation may be brought about by a rise of temperature. The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification. Ghosh and Bhattacharya¹²² found that it takes three minutes to start the photochemical reduction of tungstic acid by glucose in the presence of sunlight. The rate of reaction then increases up to eight minutes, after which it obeys a zero-molecular law. This period of induction is probably due to the fact that the aggregated molecules must first be broken up into simple molecules before the reduction begins.

It has been claimed¹²³ that alumina intended for use as an emulsifying agent in the manufacture of cosmetics, paints and cleaning agents may be improved by ripening it by ultraviolet irradiation.

In determinations of particle size in colloidal sols, it has been possible to make observations of the Tyndall cone produced by ultraviolet as well as by visible light.^{124, 125}

Effects of Irradiation on the Stability of Colloidal Systems. Ultraviolet rays cause a slight decrease in the electrophoretic migration velocity of zinc hydro-

¹¹⁸ Nordenson, H., *Kolloidchem. Beihefte*, 7, 110 (1915).

¹¹⁹ Dede, L., and Walther, T., *Ber.*, 58B, 99 (1925). For data on the effects of ultraviolet irradiation upon the growth of the particles of sulfur and of gum mastic sols, see Audubert, R., *Ann. Phys.*, 18, 5 (1922); *Chem. Abs.*, 16, 3812 (1922).

¹²⁰ Voigt, J., *Kolloid-Z.*, 43, 30 (1927); 45, 319 (1928).

¹²¹ Wassiljewa, A., *Z. wiss. Phot.*, 12, 1 (1913); *J. Chem. Soc.*, 104, ii, 265 (1913).

¹²² Ghosh, S., and Bhattacharya, A. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, 2, 29 (1932); *Chem. Abs.*, 27, 2097 (1933); Ghosh, J. C., and Banerjee, T., *Kolloid-Z.*, 86, 372 (1939).

¹²³ Dickerson, T. W., *British P.* 487,855, June 25, 1938.

¹²⁴ Lohfert, H., *Kolloid-Z.*, 51, 65 (1930).

¹²⁵ With reference to the action of ultraviolet in producing fog nuclei, see Ramsauer, C., *Ber. deut. Physik. Ges.*, 13, 899 (1911); *J. Chem. Soc.*, 102, ii, 5 (1912). On the formation of nuclei in moist air, Saltmarsh, M., *Proc. Phys. Soc.*, 27, 357 (1915).

sols, but not alcosols, according to Schaum and Friederich.¹²⁶ Light also affects the electrophoresis of silver halide hydrosols and may even reverse the direction of migration of the particles. The migrations of many other sols were not, however, affected by light in Schaum's experiments.

A number of investigators have studied the effect of ultraviolet light in altering the stability of particle size of previously prepared colloidal sols. In experiments in which silver sols prepared by the high-frequency arc method were adsorbed by filter paper and exposed to the rays, Long¹²⁷ found the more highly dispersed ones to be particularly sensitive. Wiegel¹²⁸ also noted that coagulation of dextrin-silver sols is accelerated by light, and especially the shorter wave-lengths. Galecki and Spychalski¹²⁹ found that the smaller the particles of silver nuclear hydrosols, the more readily were they decolorized by ultraviolet rays. The conductivity increases and the viscosity decreases, but these changes may be reversed on prolonged irradiation. It is suggested that the radiation causes the formation of hydrogen peroxide, which dissolves the colloidal silver and decolorizes the sol by forming silver ion. This may subsequently be reduced by the action of the ultraviolet rays. The reaction, as followed by spectrophotometry at 5100Å, appeared to be of the first order. The values of the reaction velocity constants varied at 10° from 0.0528 to 0.1345 and at 29° from 0.0875 to 0.2104 for the particular sols used. The temperature coefficient had a mean value of 1.3. According to Galecki and Marchlewska,¹³⁰ gelatin and ageing increase the time required for ultraviolet light to decolorize the sols.

The coagulation of Bredig's platinum hydrosol¹³¹ may be greatly hastened by exposure to a 220-volt Cooper-Hewitt quartz lamp at a distance of 15 cm. A platinum sol which was not completely coagulated in two years in ordinary light was half coagulated in ten hours of irradiation. Similarly, the rays accelerate the coagulating action of common salt.

Zakowski¹³² finds the induction period or period of slow growth of gold particles upon gold nuclei to be diminished by previous irradiation of the gold solution by ultraviolet light. Beaver and Muller¹³³ have reviewed the many older observations regarding the effect of light in reducing gold salts or in accelerating the action of reducing agents in the formation of colloidal gold. Nordenson¹³⁴ was convinced that the coagulating effect of the ultraviolet rays upon gold sols was not due to a photoelectric effect because the result was the same for positively and for negatively charged particles. He suggested either that the light may cause a difference of potential between adjacent particles leading to attraction and eventual precipitation, or that the light may disturb the adsorption equilibrium between particles and associated ions, leading to instability and coagulation. Beaver and Muller attempted to determine why the sensitivity of gold sols is markedly dependent upon their past history, some being entirely unaffected by ultraviolet light, while others are readily coagulated by it. Fourteen days' exposure to a 220-volt mercury arc did not affect Bredig gold sols or sols prepared by

¹²⁶ Schaum, K., and Friederich, P., *Z. wiss. Phot.*, **23**, 98 (1924); *Chem. Abs.*, **19**, 1376 (1925).

¹²⁷ Long, S. H., *Kolloid-Z.*, **14**, 136 (1914).

¹²⁸ Wiegel, E., *Z. wiss. Phot.*, **24**, 316 (1927); *Brit. Chem. Abs.*, **A1927**, 411.

¹²⁹ Galecki, A., and Spychalski, R., *Roczniki Chem.*, **8**, 394 (1928); *Z. anorg. allgem. Chem.*, **177**, 337 (1928); *Kolloid-Z.*, **53**, 338 (1930); *Chem. Abs.*, **23**, 1572 (1929); **25**, 876 (1931).

¹³⁰ Galecki, A., and Marchlewska, J., *Kolloid-Z.*, **59**, 206 (1932).

¹³¹ Spear, E. B., Jones, P. F., Neave, A. S., and Schlager, M., *J. Am. Chem. Soc.*, **43**, 1385 (1921).

¹³² Zakowski, J., *Kolloidchem. Beihefte*, **23**, 117 (1926).

¹³³ Beaver, J. J., and Muller, R. H., *J. Am. Chem. Soc.*, **50**, 304 (1928).

¹³⁴ Nordenson, H., *Z. physik. Chem.*, **90**, 603 (1915).

means of hydrazine, phosphorus, formaldehyde or acetylene. On the other hand, sols prepared by means of hydrogen peroxide, tannin, quinol, catechol, resorcinol or pyrogallol, turned blue within the first two days, the light having a slow coagulating effect. After eight days of irradiation, they turned clear red, the unstable sol being peptized to a sol identical in appearance and behavior with the one originally used. After this, light had no further effect. In the case of the tannin and hydrogen peroxide sols, the stability toward ultraviolet radiation was in general dependent upon the pH at which the reduction had originally been brought about. The sensitivity toward radiation was progressively less as neutrality was approached, and was at a minimum at slight alkalinity for the peroxide sols. In the range of pH 7.5 to 9.0, the sensitivity, although slight, varied, so that a number of the sols identical in appearance exhibited different behavior toward the light. Radiation of wave-lengths shorter than the 2150A line is required for the change from red to blue. In a tannin sol, there was a slight but definite increase of the refractive index as the sol became blue. It decreased again as the sol was peptized by the radiation. The changes were even less in a hydrogen peroxide sol. The conductivity changed in a similar manner to the extent of about 0.3 per cent. These effects were attributed to changes in the amounts of stabilizing ions adsorbed. As more ions appeared in the solution in the first part of the irradiation, fewer were adsorbed and the stability was decreased. The absorption spectrum of the sol proved one of the most sensitive indicators of the changes taking place. Conductance titrations with silver nitrate indicated an increased concentration of chloride ion in the bulk of the solution in the blue sol and a return to the original concentration in the peptized red sol. Although the original and the red final states appeared to be identical, it was evident from the photochemical indifference of the latter that they are in fact different. This was also apparent from spectrograms in the far ultraviolet, since the peptized sol no longer absorbed the effective radiation. It is possible that when peptization had been effected, the ions were more firmly associated with the complex; this would account for the greater stability toward light as well as for the lack of absorption bands in the effective region.¹³⁵

It has been shown by Murphy and Mathews¹³⁶ that the electrical conductivity of arsenic trisulfide hydrosol increases upon exposure to light, the rate of change increasing somewhat with decreasing concentration of the colloid.

According to Freundlich and Moor,¹³⁷ a mixture of silver and arsenious sulfide sols undergoes in the dark a change of color from a golden-brown through greenish-brown to lilac, and, with exposure to light, through green to a golden-brown. Both changes are prevented in the presence of a gelatin gel. The reaction in the dark is regarded as a direct interaction between the particles of the two sols. The secondary change under the action of light is purely chemical and involves oxygen and the probable formation of a silver thioarsenite. Horiba and Baba¹³⁸ find that on illumination, arsenious sulfide and Congo red sols, but not ferric or chromic hydroxide sols, exhibit increased osmotic pressure. Colloidal cuprous hydroxide, formed by boiling cuprous chloride or bromide with aqueous gelatin, is photosensitive in the presence of acid.¹³⁹

The reactions of gold and silver sols with arsenic and antimony trisulfide sols

¹³⁵ See also Thiessen, P. A., *Kolloidchem. Beihefte*, 29, 122 (1929).

¹³⁶ Murphy, R. V., and Mathews, J. H., *J. Am. Chem. Soc.*, 45, 16 (1923).

¹³⁷ Freundlich, H., and Moor, F., *Kolloid-Z.*, 36, 17 (1921).

¹³⁸ Horiba, S., and Baba, H., *J. Phys. Chem. Japan*, 3, 1 (1929); *Brit. Chem. Abs.*, A1930, 691.

¹³⁹ Horiba, S., and Ishii, S., *J. Phys. Chem. Japan*, 2, 118 (1929); *Brit. Chem. Abs.*, A1930, 691.

are photosensitive.¹⁴⁰ Rapid color change is produced by sunlight and the product is found to consist of metallic sulfides, free sulfur and arsenious or antimonious acids.

Krestinskaya¹⁴¹ found arsenious sulfide sols to be rendered more stable toward the barium ion by exposure to light. Sols of different concentrations and compositions were, however, affected differently in respect to the coagulating action of other ions. According to Joshi, Barve and Desai,¹⁴² on exposure of an arsenious sulfide sol to light, the charge on the particles decreases, the conductivity increases, the total sulfur decreases, the stability to potassium chloride passes through a maximum, and the stability to magnesium chloride decreases continuously. These effects are attributed to the hydrolysis of the sulfide to arsenious acid and hydrogen sulfide, the latter yielding sulfur dioxide, sulfur and pentathionic acid.

Boutaric and Bouchard¹⁴³ found the time of coagulation of arsenious sulfide and other sols by electrolytes in the presence of fluorescein, eosin or erythrosin, was in all cases decreased by illumination, the effect being greater in ultraviolet than in visible light freed from infrared. Potassium sulfate and sulfuric acid, which inhibit the fluorescence of the dyes, also suppress the effect of the light. The light had no effect in the absence of the fluorescent compounds, and the dyes did not affect the sols in the dark. The difference between the time required for flocculation in the dark and in daylight or ultraviolet light is proportional to the logarithm of the fluorescing power of the mixture of fluorescein and added electrolyte, if any. Tannin, hydroquinone, phenol and cresol in the presence of lithium chloride also reduce both the fluorescing power and the shortening of the flocculation time. Eosin and erythrosin which have absorption bands close to that of fluorescein, reduce its fluorescence and also reduce its effect on the flocculation time. The difference in the time required for flocculation in the dark and in ultraviolet light is reduced from 60 to 15 minutes by 0.05 per cent Direct-Scarlet solution. A number of colorless substances which fluoresce in the ultraviolet were also found effective. Among these are esculin and a number of naphtholsulfonic acids.

X-rays, ultraviolet radiations and α -rays cause the coagulation of sols of cerium hydroxide and albumin, and the inversion of cane sugar solutions, according to Fernau.¹⁴⁴

Berlin blue hydrosols are decolorized and coagulated by visible and ultraviolet light. The time of flocculation by irradiation is proportional to the layer thickness and sol concentration; the optimum wave-length is 4200Å.¹⁴⁵ Lal and Ganguly¹⁴⁶ found, however, that Prussian blue and gum mastic sols were not coagulated by the full radiation of the quartz mercury arc, although various sulfide sols (arsenic, cadmium, antimony, and ferrous), metallic sols (platinum, silver and gold), sulfur sols, hydroxides (cerium, thorium, ferric) were affected. The pH of the sols varied during exposure, some increasing and some decreasing. Coagulation was attributed to the destruction of stabilizing agents by the action of the light. These observations were extended by Miss Roy.¹⁴⁷ Sols of stannic, aluminum and

¹⁴⁰ Bhatnagar, S. S., Yajnik, N. A., and Zadoo, V. D., *Quart. J. Indian Chem. Soc.*, **4**, 209 (1927); *Chem. Abs.*, **21**, 3514 (1927).

¹⁴¹ Krestinskaya, V., *Kolloid-Z.*, **66**, 58 (1934); *Chem. Abs.*, **28**, 1909 (1934).

¹⁴² Joshi, C. B., Barve, P. M., and Desai, B. N., *Current Sci.*, **3**, 105 (1934); *Chem. Abs.*, **29**, 22 (1935).

¹⁴³ Boutaric, A., and Bouchard, J., *Compt. rend.*, **192**, 95, 357 (1931); **193**, 45 (1931); **194**, 1245 (1932); *Bull. Soc. Chim.*, **51**, 757 (1932); Pospelov, A., and Pospelova, K., *J. Phys. Chem. (U.S.S.R.)*, **5**, 52 (1934); *Chem. Abs.*, **28**, 4315 (1934).

¹⁴⁴ Fernau, A., *Kolloid-Z.*, **33**, 89 (1923); *Chem. Abs.*, **17**, 3837 (1923).

¹⁴⁵ Lederer, E. L., and Hartleb, O., *Kolloid-Z.*, **62**, 42 (1933); *Chem. Abs.*, **27**, 1800 (1933).

¹⁴⁶ Lal, P., and Ganguly, P. B., *J. Indian Chem. Soc.*, **6**, 547 (1929); *Chem. Abs.*, **24**, 540 (1930).

¹⁴⁷ Roy, S., *J. Indian Chem. Soc.*, **6**, 431 (1929); *Chem. Abs.*, **23**, 4865 (1929).

thorium hydroxides, of antimony, arsenious and mercuric sulfides, acquired increased conductivity after exposure, although uranium and cupric ferrocyanide sols did not. She found a short exposure to increase the stability of arsenious and antimony sulfides and uranium and cupric ferrocyanides, but on longer exposure all became less stable, and sols of antimony sulfide, mercuric sulfide and uranium ferrocyanide coagulated completely.

Heller¹⁴⁸ has considered the case in which the photochemical action is on the adsorbed electrolyte; coagulation is then probably due to the critical diminution of the double layer and the effect of light should be expected to be greater as the double layer is initially weaker. Sols of ferric oxide obtained by hydrolysis of ferric nitrate were dialyzed for three to twenty-five days and examined magnetooptically after varying periods in darkness followed by exposure to diffused light. The rate of growth of size of particles decreased with the time in darkness, but increased again on exposure to light, the increase being greatest in the sols longest dialyzed and so least stable.

Emulsions of benzene, benzine and carbon disulfide in water with sodium oleate as the emulsifier separated into two layers when irradiated with ultraviolet light.¹⁴⁹ The pH of the illuminated emulsion increased, indicating that its breaking was due to the partial destruction of the emulsifying agent.

Effects of Irradiation on Liesegang Ring Formation. Light of short wavelength is reported by Davies¹⁵⁰ to aid in the production of colored bands of colloidal gold in silicic acid gels containing gold chloride and various reducing agents. The work was extended by Cadenhead¹⁵¹ to include the effects of x-rays. Both workers agree that the banding on reduction to colloidal gold is not a true Liesegang phenomenon. It has been observed¹⁵² that the passage of a beam of light through soil or kaolin suspensions contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between the successive strata appears to vary with the wave-length of the light, but the strata produced by white light are quite sharp. The stratification persists while the illumination is continued, and slowly disappears when it is cut off.

Blair¹⁵³ points out that in gels in either intense white light or complete darkness there is irregular Liesegang ring formation, which persists even after liquefaction and resetting. Ultraviolet rays from a quartz mercury lamp in a few hours render a gel incapable of Liesegang ring formation, but this effect does not persist after liquefaction.

Ultraviolet radiations cause a marked disturbance¹⁵⁴ in the rings formed round a drop of silver nitrate solution placed on a film of setting gelatin. X-rays and radium have no effect. The radiation restrains the primary rings and prevents the formation of secondary ones.¹⁵⁵ In the case of silver chromate-gelatin,¹⁵⁶ visible light causes the number of bands to increase and the distance between them

¹⁴⁸ Heller, W., *Compt. rend.*, 199, 723 (1934).

¹⁴⁹ Sinha, P. C., and Ganguli, P. B., *Kolloid-Z.*, 54, 147 (1931).

¹⁵⁰ Davies, E. C. H., *J. Am. Chem. Soc.*, 45, 2261 (1923).

¹⁵¹ Cadenhead, A. F. G., *Can. Chem. Met.*, 10, 201 (1926); *Chem. Abs.*, 20, 3390 (1926).

¹⁵² Morrison, C. G. T., *Proc. Roy. Soc. London*, 108A, 280 (1925).

¹⁵³ Blair, G. W. S., *Phil. Mag.*, 49, 90 (1925).

¹⁵⁴ Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, 104, 1001 (1930); *Chem. Abs.*, 25, 3245 (1931); see also Hatschek, E., *Kolloid-Z.*, 37, 297 (1925); *Proc. Roy. Soc. London*, 96A, 496 (1921) for similar observations on lead chromate bands.

¹⁵⁵ Kofman, T., *J. chim. phys.*, 29, 586 (1932); *Compt. rend.*, 208, 567 (1939).

¹⁵⁶ Isemura, T., *Bull. Chem. Soc. Japan*, 8, 108 (1933); *Chem. Abs.*, 27, 4152 (1933); Taboury, M.-F., and Bellot, M., *Compt. rend.*, 205, 45 (1937). See also Teft, R., and Hill, J. W., *Trans. Kansas Acad. Sci.*, 33, 57 (1931) for some effects of light on the formation of banded precipitates of mercuric iodide.

to shorten. Ultraviolet rays retard the formation of rings, which are finer and closer together than in the dark. Nikiforov and Lemeche¹⁵⁷ believe the "pressure" of Liesegang rings directly proportional to the light intensity. The number of rings per unit of distance increases under both ultraviolet and diffused daylight. Similar observations have been recorded by Miyamoto.¹⁵⁸ Chloride ions in definite concentrations seem to be necessary for light to have an effect on the production of the rings.¹⁵⁹

It is held by Alekseevskii¹⁶⁰ that the adsorptive power of active charcoal and of silica gel is increased by irradiation with ultraviolet rays.

¹⁵⁷ Nikiforov, V.-K., *J. chim. phys.*, **32**, 585 (1935). Nikiforov, V.-K., and Lemèche, M.-R., *Ibid.*, **33**, 250 (1936).

¹⁵⁸ Miyamoto, S., *Kolloid-Z.*, **78**, 23 (1937).

¹⁵⁹ Köhn, M., and Mainzhausen, L., *Kolloid-Z.*, **79**, 316 (1937).

¹⁶⁰ Alekseevskii, E. V., *J. Russ. Phys.-Chem. Soc.*, **60**, 1173 (1928); *Chem Abs*, **23**, 2367 (1929).

Chapter 22

The Reactions of Organic Compounds. Aliphatic Series¹

A very considerable body of empirical information has been accumulated regarding the photochemical behavior of a wide range of organic compounds, in large part due to the pioneering observations of Ciamician and Silber on the effects of prolonged exposures to sunlight and of Berthelot and Gaudechon on the effects of ultraviolet light. Unsaturated hydrocarbons rayed with ultraviolet undergo stereoisomeric transformations or polymerize. Alcohols, aldehydes and ketones decompose into carbon monoxide, hydrogen and hydrocarbons under some conditions. Acids may yield carbon dioxide and a hydrocarbon, with some carbon monoxide and hydrogen. Dibasic acids readily lose carbon dioxide, leaving mono-basic acids. Keto acids react in ultraviolet when heated.

The theoretical interpretations of this behavior and its relation to the absorption spectra of the compounds studied has been most advanced in the case of the aldehydes and of the interconversions of geometrical isomers.

SATURATED HYDROCARBONS

The ultraviolet absorption spectra of the saturated hydrocarbons lies in the extreme ultraviolet. This accounts for the observed inertness of these compounds to the ordinarily available ultraviolet radiations.²

Methane is unaffected by the radiations between 2300 and 4000A.³ With a Harteck xenon lamp giving 3×10^{16} quanta per second, the 1469A line is 13 per cent and the 1295A line 100 per cent absorbed by a 30-mm. layer of the gas at atmospheric pressure.⁴

The methane is decomposed in the primary process into methyl radicals and hydrogen atoms, the final products being hydrogen and acetylene, traces of ethylene, ethane and hydrocarbons with three to five carbon atoms.

Leighton and Steiner⁵ also state that the radiation from a hydrogen discharge tube transmitted by a thin fluorite window decomposes methane with a quantum yield of the order of unity. They identified hydrogen and possibly ethylene in the approximate molecular ratio of four to one.

According to Tolloczko,⁶ ethane irradiated in quartz with rays of wave-lengths between 2300 and 4000A gave a small amount of a light colorless condensate, composed of a mixture of hydrocarbons, mostly hexane; the gas contained hydro-

¹ For a general review, see Bonhoeffer, K. F., *Z. Elektrochem.*, **40**, 425 (1934).

² Glockler, G., *Proc. Nat. Acad. Sci.*, **11**, 74 (1925); Kemula, W., and Mrazek, S., [*Compt. rend.*, **195**, 1004 (1932)] found methane, ethane and butane not to absorb between 6000 and 1965A.

³ Tolloczko, S., *Przemysł Chem.*, **11**, 245 (1927); *Chem. Abs.*, **22**, 4380 (1928).

⁴ Groth, W., and Laudenklaus, H., *Naturwiss.*, **24**, 796 (1936); Groth, W., *Z. physik. Chem.*, **B38**, 366 (1937); see also Kemula, W., and Dyduszyński, A., *Roczniki Chem.*, **17**, 423 (1937); *Brit. Chem. Abs.*, **A**, 39 (1938).

⁵ Leighton, P. A., and Steiner, A. B., *J. Am. Chem. Soc.*, **58**, 1823 (1936).

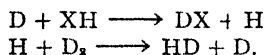
⁶ Tolloczko, S., *loc. cit.*

gen and methane. Klemenc and Patat⁷ claim that pentane suffers decomposition and polymerization. The polymerization products take up oxygen, breaking the carbon chain and producing methane and carbon monoxide and dioxide.

Because of their transparency to ultraviolet rays, the liquid hydrocarbons are especially suitable solvents for use in measuring the absorption spectra of various organic solutes. Castille and Henri⁸ have given detailed directions for the purification of hexane for this purpose. Samples of hexane prepared by their methods transmitted, in 40-mm. layers, to 1900Å. Butane prepared by the Grignard method may contain an unidentified substance which shows fifteen absorption bands between 2206 and 1965Å.⁹ This impurity can be removed by long agitation with bromine water. In the Schumann regions, heptane and hexane have an absorption maximum at 1500Å.¹⁰ In the unsaturated compounds 1-heptylene, 2-pentylene, 1-pentylene, trimethylethylene, this is shifted to 1750Å. These bands are without fine structure and are attributed to the dissociation of a carbon-carbon bond. Duncan and Howe¹¹ state that methane shows true continuous absorption in the region between 1450 and 850Å, such continuous spectra being general for molecules with tetrahedral symmetry.

Mercury-sensitized reactions of ethane have recently been described by Kemula, Mrazek and Tolloczko.¹² Butane, hexane and octane are formed together with traces of methane. The proportion of butane in the product varies directly with the rate of flow and the pressure of the ethane, and inversely with the temperature of the receiver. Both the carbon-carbon and carbon-hydrogen linkings are affected. When butane is removed by a low-temperature trap, the reaction products, according to Steacie and Phillips, are exclusively methane, propane and butane. The quantum yield for ethane decomposed is 0.2.¹³

Taylor, Morikaw and Benedict¹⁴ found that methane reacts with deuterium at 40° to 300°C. in the presence of mercury vapor excited by its resonance radiation. The degree to which the substitution occurs depends upon the time and temperature of irradiation. Farkas and Melville¹⁵ proposed a chain mechanism for the reaction at temperatures over 300°C.:



The oxidation of methane, methyl chloride and methylene chloride may be sensitized to light of the wave-length 4360Å by chlorine.¹⁶ The products from each of these compounds include carbon monoxide and hydrogen chloride, as well as small amounts of water, phosgene and several heavy volatile organic compounds. The quantum yield varies from 80 for methane to 800 for methylene chloride.

⁷ Klemenc, A., and Patat, F., *Z. physik. Chem.*, **149A**, 449 (1930); see also Landau, M., *Compt. rend.*, **155**, 403 (1912); *J. Chem. Soc.*, **102**, II, 986 (1912).

⁸ Castille, A., and Henri, V., *Bull. Soc. chim. biol.*, **6**, 299 (1924); the observations of Urbain, E., and Scal, C., [*Compt. rend.*, **168**, 887 (1919)] on the decomposition of saturated liquid hydrocarbons by ultraviolet rays may have been due to the presence of impurities.

⁹ Kemula, W., and Mrazek, S., *loc. cit.*

¹⁰ Carr, E. P., and Stücklen, H., *Helv. Phys. Acta*, **6**, 261 (1933).

¹¹ Duncan, A. B. F., and Howe, J. P., *J. Chem. Physics*, **2**, 851 (1934).

¹² Kemula, W., Mrazek, S., and Tolloczko, S., *Chem. Listy*, **26**, 466 (1932); *Chem. Abs.*, **27**, 3142 (1932).

¹³ Steacie, E. W. R., and Phillips, N. W. F., *J. Chem. Phys.*, **6**, 179 (1938).

¹⁴ Taylor, H. S., Morikaw, K., and Benedict, W. S., *J. Am. Chem. Soc.*, **57**, 383 (1935); *J. Chem. Phys.*, **5**, 212 (1937).

¹⁵ Farkas, A., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 625 (1936).

¹⁶ Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **177A**, 245 (1936).

These are all chain reactions, involving the formation of intermediate, short-lived peroxides. Methane and methyl chloride also suffer chlorination to methylene chloride, some molecules of which on colliding with chlorine atoms form the CHCl_2 radical. This, reacting with oxygen, goes through various intermediate compounds to carbon monoxide and hydrogen chloride. The reactions of methane and methyl chloride, but not that of methylene chloride, are inhibited by an excess of oxygen.¹⁷

Cyclopropane undergoes a mercury-sensitized photochemical polymerization to a colorless oil of high boiling point under the influence of the resonance line of mercury.¹⁸ The I. G. Farbenindustrie A.-G.¹⁹ claims the conversion of cyclohexanone into caproic acid by irradiation.

ALKYL HALIDES

Absorption Data. The absorption of methane is gradually shifted to longer wave-lengths as the number of halogen atoms introduced is increased.²⁰ However, most alkyl halides absorb but slightly. The bromides absorb more and at longer wave-lengths than the chlorides, methyl bromide absorbing nearly as well as carbon tetrachloride. The foot of the absorption curve of carbon tetrabromide approaches the visible spectrum. The iodine compounds absorb still more readily, iodoform absorbing in the visible portion of the spectrum.

Herzberg and Scheibe²¹ found methyl iodide, bromide and chloride to show continuous absorption bands, with maxima at 2500, 2000, and 1750A, attributed to dissociation of the molecule into the methyl group and a halogen atom, one of the products being in an excited state. Iredale and Mills²² found the energies of the carbon-to-iodine and carbon-to-bromine linkings, as calculated from the long wave-length limits of the continuous bands, to be in good agreement with the values calculated from the heats of combustion.²³

Hukumoto,²⁴ who made similar calculations, reported data on the continuous absorption spectra of about forty alkyl halides. The iodides exhibited two or three absorption regions, the one with longest wave-lengths corresponding to a decomposition into a normal alkyl radical and an iodine atom in the metastable $2^2\text{P}_{1/2}$ state. The excess energy in the second and third continuous absorption regions was thought to be associated with excitation of the alkyl radicals.

Parti and Samuel²⁵ interpret the absorption spectrum of methyl iodide as involving a simultaneous loss of a hydrogen and an iodine atom. They pointed out that the beginnings of the first selective absorption of twelve alkyl halides agree with the estimated energy differences $D(\text{CX}_4) - D(\text{CX}_2)$. This viewpoint, based on an analogy with the behavior of the tin halides, appears to involve a consid

¹⁷ Schumacher, H. J., *Z. Elektrochem.*, **42**, 522 (1936).

¹⁸ Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

¹⁹ I. G. Farbenindustrie A.-G., British P. 314,267, 1928.

²⁰ Lowry, T. M., and Sass, R. B., *J. Chem. Soc.*, 622, 1926.

²¹ Herzberg, G., and Scheibe, G., *Trans. Faraday Soc.*, **25**, 716 (1929), *Z. physik. Chem.*, **7B**, 390 (1930).

²² Iredale, T., and Mills, A. G., *Proc. Roy. Soc.*, **133A**, 430 (1931). See also *Z. physik. Chem.*, **20B**, 340 (1933).

²³ For details of the calculation of the heats of dissociation of the carbon-halogen bond by this method, see also Sen-Gupta, P. K., *Bull. acad. Sci. United Provinces Agra Oudh, India*, **2**, 115 (1933); *Chem. Abs.*, **27**, 3668 (1933).

²⁴ Hukumoto, Y., *Phys. Rev.*, **42**, 313 (1932); *Science Repts. Tohoku Imp. Univ. First Ser.*, **22**, 13 (1933); **21**, 906 (1932). Data on methyl bromide are given by Fink, P., and Goodeve, C. F., *Proc. Roy. Soc.*, **A163**, 592 (1937).

²⁵ Parti, Y., and Samuel, R., *Current Sci.*, **5**, 386 (1937); *Chem. Abs.*, **31**, 3385 (1937); Bergmann, E., and Samuel, R., *Nature*, **141**, 832 (1938).

erable revision of the current theories of the photochemical processes in which the alkyl halides participate.

As determined by Saha,²⁶ who obtained the limit of continuous absorption from spectrograms by the method of Herzberg and Scheibe, the wave-length limits and their values in kcal. for the C—Cl bond are in carbon tetrachloride, 2800Å, 102, in chloroform, 2660Å, 107.5, and in methylene chloride, 2500Å, 114.4 kcal. These results are considered as in good agreement with those calculated thermochemically, if allowance be made for uncertainty as to the energy state of the carbon atom.²⁷

The alkyl halides also exhibit discontinuous absorption beginning at 2010, 1785 and 1600Å for methyl iodide, bromide and chloride, respectively, according to Herzberg and Scheibe.²⁸ The discontinuous bands are considered to indicate transitions into several excited electronic states.²⁹

Reactions. Although early observers made frequent reference to the decomposition of alkyl halides in light,³⁰ Stobbe and Schmitt³¹ showed that the effects noted in daylight were due to an oxidation. In the absence of oxygen the halides are relatively light-stable. They did, however, show that a photochemical liberation of bromine from ethyl bromide occurs in the short wave length ultraviolet to a slight extent. Similar reactions occur also with the iodides, isopropyl iodide being less stable than either *n*-propyl, ethyl or methyl iodides.

The products formed when ethyl iodide is photochemically decomposed in the absence of oxygen include, according to Emschwiller and Job,³² besides iodine, a gas composed principally of ethylene and ethane, with smaller amounts of butane and hydrogen. The formation of the butane could be explained as due to a combination of two ethyl radicals liberated in the primary process. The ethylene and ethane were accounted for by assuming that the primary process for the most part consists in a simultaneous loss of both hydrogen and iodine atoms from the ethyl iodide as hydrogen iodide, leaving ethylene. (The ethane might then arise by combination of ethylene with hydrogen produced by the photodecomposition of the hydrogen iodide.³³) In similar fashion, propyl iodide yielded propylene and propane, normal, secondary and isobutyl iodides gave butylene and butane, and methyl iodide gave methane. Tertiary butyl iodide gave propylene and propane, ethylene and ethane. In these experiments the alkyl halides were irradiated as liquids. Emschwiller believed both the hydrogen and the iodine atoms to be liberated from the same carbon atom, the residue rearranging to give the olefine. He also believed studies of the photochemical oxidation of the alkyl halides to corroborate this conception, methyl iodide, ethyl iodide and isopropyl iodide giving formaldehyde, acetaldehyde and acetone, respectively.³⁴ It may be noted that Emschwiller's conception of the primary process is in agreement with that of Parti

²⁶ Saha, N. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, 2, 233 (1933); *Chem. Abs.*, 27, 4733 (1933). For further data on other halides, see Reisman, R. A., Samuel, R., and Sharf-ud-Din, *Indian J. Physics*, 8, 537 (1934); Price, W. C., *Phys. Rev.*, 47, 419 (1935); *J. Chem. Physics*, 3, 365 (1935); 4, 547 (1936).

²⁷ For the absorption spectra of more complex halides, see Fukumoto, Y., *Science Repts., Tohoku Imp. Univ. First Series*, 23, 62 (1934).

²⁸ Also Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, 20B, 283 (1933).

²⁹ See also Henrici, A., *Z. Physik*, 77, 35 (1932) and for the theoretical interpretation of the methyl iodide bands, Mulliken, R. S., *Phys. Rev.*, 47, 413 (1935), and Porret, D., and Goodeve, C. F., *Trans. Faraday Soc.*, 33, 690 (1937); *Proc. Roy. Soc.*, A165, 31 (1938).

³⁰ Schoorl, N., and Van den Berg, L. M., *Pharm. Weekblad*, 43, 218 (1906); Benrath, A., *Annalen*, 382, 222 (1911).

³¹ Stobbe, H., and Schmitt, P., *Z. wiss. Phot.*, 20, 57 (1920).

³² Emschwiller, G., and Job, A., *Compt. rend.*, 179, 52, 168 (1924).

³³ Emschwiller, G., and Job, A., *Compt. rend.*, 192, 799 (1931); 193, 1003 (1931).

³⁴ Emschwiller, G., and Job, A., *Ann. Chim.*, 17, 413 (1932).

and Samuel, although the latter workers do not postulate a rearrangement of the radical with divalent carbon to an olefin.

On the other hand, Bates and Spence³⁵ believe the primary process, at least, in the case of gaseous methyl iodide, to consist solely in a simple dissociation into a free methyl radical and an iodine atom.³⁶ They also support this by a study of the reaction occurring in the presence of oxygen. In this case the methyl radical may react with oxygen to produce formaldehyde and an hydroxyl radical. The latter, on reaction with a fresh methyl iodide molecule yields methanol and an iodine atom. Methanol (two molecules) and formaldehyde may then react to produce methylal, $(\text{CH}_3\text{O})_2\text{CH}_2$, and water. Furthermore, Spence and Wild³⁷ found the irradiation of pure methyl iodide in the absence of oxygen to yield no hydrogen iodide. Small amounts of methane, ethane and iodine were formed.³⁸ The presence of free methyl radicals in the photochemical decomposition of methyl iodide vapors has been recently demonstrated by the ortho-para hydrogen conversion test for the presence of paramagnetic substances.³⁹

In his earlier work, Emschwiller⁴⁰ believed that a critical threshold wave-length for the ethyl iodide and methyl iodide decompositions had been observed at 4100Å. In later observations, however, he gave up the concept of the existence of a threshold value since he had found the absorption curve of ethyl iodide to vary with the temperature, being shifted toward the visible by about 12Å per 10°C.⁴¹

The quantum yields obtainable under various conditions have been a matter of controversy. Bates and Spence⁴² found that methyl iodide vapors, when irradiated in the continuum, gave the very low quantum yield of 0.02. It was slightly greater (0.05) in hexane solution. Spence and Wild⁴³ put the yield of methane from methyl iodide vapor at 0.032, that of free iodine being half as great. Calculated as methyl iodide destroyed, the quantum yield is at least 0.06. Higher iodides are probably formed. The reaction is not affected by the addition of hydrogen or nitrous oxide.

Very similar results have been recorded for ethyl iodide, although Emschwiller gave yields at high temperatures for ethyl iodide seventeen or more times as great as for methyl iodide. Norton⁴⁴ found for liquid ethyl iodide the values 0.315 at 3130Å, 0.38 at 2654Å and 0.41 at 2537Å. The higher yields of about unity reported by Iredale were believed to have been due to the presence of some oxygen.⁴⁵

³⁵ Bates, J. R., and Spence, R., *J. Am. Chem. Soc.*, **53**, 381, 1689 (1931), *Trans. Faraday Soc.*, **27**, 468 (1931).

³⁶ A general discussion of free radicals in organic photoprocesses is due to H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

³⁷ Spence, R., and Wild, W., *Proc. Leeds Phil. Lit. Soc., Sci. Section*, **3**, 141 (1936), *Chem. Abs.*, **30**, 2849 (1936). In the presence of hydrogen iodide, methyl iodide yields iodine with a quantum yield of two, according to Iredale, T., and Stephan, D., *Trans. Faraday Soc.*, **33**, 800 (1937).

³⁸ Jones, L. T., and Bates, J. R., [*J. Am. Chem. Soc.*, **56**, 2285 (1934)] found the kinetics of the rapid photooxidation of ethyl iodide to differ from that of methyl iodide. Acetaldehyde and ethanol were produced. A mechanism involving the intermediary formation of ethyl peroxide was proposed, but the observation of small deviations in the rates from those expected suggested the reaction to be one of great complexity.

³⁹ West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935). It also is found in the acetone decomposition, but negative tests were obtained in the irradiation of benzene and of propionaldehyde vapors.

⁴⁰ Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52,168 (1924).

⁴¹ Job, A., and Emschwiller, G., *Compt. rend.*, **190**, 741,866 (1930); *Ann. Chim.*, **17**, 413 (1932).

⁴² Bates, J. R., and Spence, R., *J. Am. Chem. Soc.*, **53**, 1689 (1931).

⁴³ Spence, R., and Wild, W., *Proc. Leeds Phil. Lit. Soc., Sci. Section*, **3**, 141 (1936); *Chem. Abs.*, **30**, 2849 (1936).

⁴⁴ Norton, B. M., *J. Am. Chem. Soc.*, **56**, 2294 (1934).

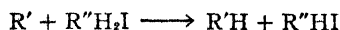
⁴⁵ Iredale, T., *J. Phys. Chem.*, **33**, 290 (1929). It must be noted, however, that Gibson, K. E., and Iredale, T., [*Trans. Faraday Soc.*, **32**, 571 (1936)] have found a value of unity for benzene solutions of methyl iodine in the absence of oxygen in recent redeterminations. The same value was given by γ -butyl iodide. In alcohol, methyl iodide gave values greater than one. Furthermore, iodoform in benzene gave a value of one in the absence of oxygen and higher in its presence. In alcohol, the yields seemed higher.

West and Paul⁴⁶ found the quantum yields in hexane to be a constitutive property of the alkyl group,⁴⁷ varying from a few hundredths in the case of methyl iodide to slightly over one for isopropyl iodide for the wave-length 2610A.^{47a} The yield increases somewhat with decreasing wave-lengths between 3130 and 2610A, the ratios differing, however, for each of five iodides studied. They concluded a direct recombination of the iodine atom and the free radical to be the cause of the low yield for methyl iodide. (The non-dependence of the yield on the concentration made it seem that the reaction $\text{CH}_3 + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_6 + \text{I}$ is uncommon. Similarly, the reaction between an iodine molecule and a free methyl radical was thought to be infrequent because of the zero order of the reaction in its early stages.) Accordingly, it was suggested that the values of the quantum yields shown by the various halides might give directly the relative probabilities of recombination of the various alkyl radicals with atomic iodine. If this be admitted, the order of reactivity of the alkyl radicals would be methyl > allyl > vinyl > ethyl > propyl > isopropyl.

West and Ginsburg⁴⁸ found that, although in the pure liquid state or in hexane solution, ethyl iodide decomposes with a quantum yield of 0.6, in the vapor state the quantum yields at 2600A in the continuum are very low.

They also made observations of the quantum yields at the beginning of the short wave-length region of banded absorption at 2026A. In the vapor at 45 or 90 mm. pressure at 30°C., the yield was 0.1. At 0.1 mm. it was definitely lower, and was also lower than that of the reaction produced by this wave-length in condensed phases, the yield in the liquid being about 0.24. In the short wave-length region, interaction between excited molecules and normal molecules seemed the predominant mechanism.

Especial attention was paid, by West and Schlessinger,⁴⁹ to the products other than iodine. They found that at 2537A methyl iodide yields mostly methane and small quantities of ethylene and ethane, and that more than a third of the iodide decomposed appears as methylene iodide. Addition of silver foil increases the rate of reaction about fortyfold, yields all the iodine as silver iodide, and causes the gaseous products to consist mostly of ethane with some ethylene but much less methane than in the absence of silver. Ethyl iodide at 2537A gives ethane and ethylene in comparable proportions. At 2026A, small amounts of methane and hydrogen are also formed. Silver increases the reaction rate but does not affect the nature of the products. Inert gas up to 40 atmospheres increases the iodine yield linearly with the density of inert gas to values approaching one-third the yield in inert liquid solvents. The primary process forms iodine atoms and alkyl radicals. Recombination of these, which may occur as a bimolecular process, is the most rapid secondary process and accounts for the low quantum yields. Most of the net change is due to the reaction:



This predominates over the association of R to R_2 and I to I_2 . The quantum yield of *n*-propyl iodide vapor at 2026A is lower than that of ethyl iodide; the yields for isopropyl iodide at 2610 and 2026A are 0.17 and 0.43, respectively.

⁴⁶ West, W., and Paul, B., *Trans. Faraday Soc.*, **28**, 688 (1932).

⁴⁷ Note also Burke, K. A., and Donnan, F. G., *J. Chem. Soc.*, **85**, 574 (1904).

^{47a} Norton also notes that the quantum yield increases in various alkyl halides as the chain is lengthened, as the central carbon atom is altered from primary to tertiary and as halogen atoms are progressively introduced.

⁴⁸ West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56**, 2626 (1934).

⁴⁹ West, W., and Schlessinger, L., *J. Am. Chem. Soc.*, **60**, 961 (1938).

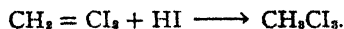
According to Maynard,⁵⁰ the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If the latter is irradiated together with methyl iodide, methyl mercuric iodide is formed rapidly. Although the action of metallic mercury is not encountered in the case of the other alkyl halides, the use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide.

Ramart-Lucas and Salmon-Legagneur⁵¹ find ultraviolet light capable of converting isobutyl bromide into *tert*-butyl bromide, and propyl bromide into isopropyl bromide without any trace of dissociation occurring.

Irradiation of the vapor of methylene iodide and oxygen by the quartz mercury arc yields such products as carbon monoxide, hydrogen, iodine, formaldehyde, formic acid and ethylene glycol. The quantum yield with respect to iodine is 1.45 for light of wave-length 3100Å. Gregory and Style⁵² suggest CH_2 , CH_2O_2 and $(\text{CH}_2\text{O})_2$ as intermediates, the two latter substances changing into formic acid and formaldehyde, respectively. Emschwiller⁵³ finds iodine pentoxide to be formed particularly while some of the methylene iodide remains unattacked; it may result through the intermediary formation of peroxides of formaldehyde, formic acid, or possibly of methylene iodide.

According to Kaufmann,⁵⁴ *trans*- and *cis*- α,β -diiodoethylene and α,α' -diiodoethylene are decomposed with liberation of iodine when their ether solutions are exposed to ultraviolet, the velocity of the reaction in the first being approximately twice as great as that in the other two cases.

Solutions of ethylene iodide in carbon tetrachloride begin to absorb at 3600Å, the absorption increasing at shorter wave-lengths. DeRight and Wiig⁵⁵ found the rate of the direct decomposition due to the absorption of the wave-lengths 3130 and 3030Å approximately proportional to the absorbed energy. It increased slightly with increasing concentrations of the ethylene iodide, reached a definite maximum after the attainment of a certain amount of decomposition, and was reduced by the addition of iodine. The primary decomposition was assumed to yield atomic iodine and $\text{C}_2\text{H}_4\text{I}$. The quantum yield was 0.76 and the temperature coefficient 1.05. Emschwiller⁵⁶ observed⁵⁷ that vinyl iodide, irradiated 124 hours by a mercury vapor lamp, gave acetylene, ethylene and iodine and, in the presence of oxygen, also formed droplets of liquid containing formic acid, formaldehyde and $\text{CH}_2\text{OH}\cdot\text{CHO}$. He suggested a different mechanism for the decomposition of asymmetrical ethylene diiodide:



He also found that although $\text{CHI}=\text{CHI}$ is not oxidized in ultraviolet light, its asymmetrical isomer is completely oxidized with the formation of formic acid, a

⁵⁰ Maynard, J. L., *Science*, **56**, 492 (1922).

⁵¹ Ramart-Lucas, Mme., and Salmon-Legagneur, F., *Compt. rend.*, **186**, 39 (1928); see also Emschwiller, G., *Ann. Chim.*, **17**, 413 (1932).

⁵² Gregory, R. A., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 724 (1936).

⁵³ Emschwiller, G., *Compt. rend.*, **206**, 746 (1938).

⁵⁴ Kaufmann, H. P., *Ber.*, **55**, 249 (1922).

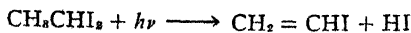
⁵⁵ DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 2411 (1935).

⁵⁶ Emschwiller, G., *Compt. rend.*, **198**, 1151 (1934).

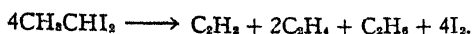
⁵⁷ Emschwiller, G., *Compt. rend.*, **198**, 464 (1934).

trace of formaldehyde, iodine and a gas composed of 57 per cent carbon monoxide, 23 per cent carbon dioxide and 20 per cent acetylene.

An iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride is discussed by Dickinson and Nies.⁵⁸ Emschwiller⁵⁹ writes for the decomposition of diiodoethane,



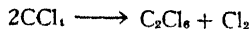
Both products then decompose with the separation of iodine, so that the complete reaction may be written:



The ethylene then mostly forms ethylene iodide. In the presence of oxygen, both diiodoethane and unsymmetrical diiodoethylene are completely oxidized. The analogy of structure between diiodomethane and diiodoethane implied by a similarity of decomposition is confirmed by the similarity of their absorption spectra and by the rapid photochemical oxidation of diiodomethane.

Iodoform, although said to be very light-stable in the absence of oxygen, may in benzene solution yield some iodine and hydriodic acid in daylight.⁶⁰ Chloroform is also stable, although it exhibits a continuous absorption beginning at 2530Å (1 cm. of liquid) or at 2300Å (50 cm. of vapor at 1 mm.). Hill⁶¹ was unable to detect any decomposition in a static system. In streaming vapor, chlorine could not be detected, but hydrogen chloride was formed. There was evidence of a short-chain reaction, yielding four molecules per quantum absorbed. The yield was not affected by the presence of hydrogen. It seemed to be increased by nitrogen and was very greatly increased by oxygen, but in the latter case the mechanism is doubtless changed. Binz and Hughes⁶² have suggested that sodium triiodomethanesulfonate, proposed for x-ray work in urological diagnosis, may owe its observed toxicity to the ease with which it splits off iodine in light.

Carbon tetrachloride has been suggested as an actinometric compound for standardizing the ultraviolet output of mercury arcs,⁶³ at wave-lengths less than about 2650-2750Å, but Hymas⁶⁴ could not obtain satisfactory results with it. According to Benrath and Hertel,⁶⁵ decomposition may be represented as



the reaction occurring in the liquid exposed in an open vessel. In a recent investigation, Lyons and Dickinson⁶⁶ found that in the absence of oxygen, pure carbon tetrachloride underwent practically no decomposition when exposed to the 2537Å line, the quantum yields being less than 0.01. In the presence of oxygen, however, phosgene and chlorine were produced in equimolar proportions, the quantum yield being close to unity.

⁵⁸ Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).

⁵⁹ Emschwiller, G., *Compt. rend.*, **199**, 854 (1934).

⁶⁰ Dubrisay, R., and Emschwiller, G., *Compt. rend.*, **195**, 660 (1932).

⁶¹ Hill, D. G., *J. Am. Chem. Soc.*, **54**, 32 (1932); see also Massol, G., and Faucon, A., *Compt. rend.*, **159**, 314 (1914); *Bull. soc. chim.*, **19**, 350 (1916).

⁶² Binz, A., and Hughes, B., *Ber.*, **68B**, 1513 (1935).

⁶³ MacKenzie, T. C., and King, A. A., "Practical Ultraviolet Light Therapy," New York, Wood 1926.

⁶⁴ Hymas, F. C., *Quart. J. Pharm.*, **2**, 281 (1929).

⁶⁵ Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

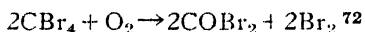
⁶⁶ Lyons, E. H., Jr., and Dickinson, R. G., *J. Am. Chem. Soc.*, **57**, 443 (1935).

Trichloroethylene may be oxidized in the presence of chlorine as sensitizer by the 4360A line.⁶⁷ The yield of dichloroacetyl chloride is not greater than 95 per cent. The rate varies with the light intensity, but is independent of the trichloroethylene and oxygen concentrations. The quantum yield is about 40 at 95°. A peroxide, $C_2HCl_4O_2$, may be a part of the chain.

In the case of tetrachloroethane,⁶⁸ the reaction probably consists in a primary decomposition into HCl and $CHCl_2CCl$, the latter then reacting with oxygen to form dichloroacetyl chloride, which is hydrolyzed by moisture to dichloroacetic acid. Oxygen also removes a hydrogen atom from the original halide, and the $CHCl_2CCl_2$ residues combine to form octachlorobutane. In dry air, a fuming liquid, dichloroacetyl chloride, could be obtained. The reactions were shown not to be due to ozone produced by the action of the light upon the oxygen. In the presence of nitrogen rather than air, no reaction whatever occurred, not even the evolution of hydrogen chloride.⁶⁹ The same was true of the compounds $CHCl_2CCl_3$ and $CCl_2=CHCl$. The reaction was therefore assumed to be brought about by activated oxygen. Further evidence for this mechanism is found in the fact that the compound $(CH_2Cl)_2$ can react, although it does not absorb in the wave-length range employed. In the presence of dry oxygen in short wave-length light, it gives monochloroacetic acid.⁷⁰

Attention has been called to a bromine-sensitized photochemical decomposition of dibromotetrachloroethane by Carrico and Dickinson.⁷¹ It proceeds as a chain reaction with quantum yields which, at low intensities, are independent of the intensity, but which fall off at higher intensities.

There is a bromine-sensitized oxidation of carbon tetrabromide in carbon tetrachloride, produced by the 4360A line, which may be expressed by



Not more than 50 kcal. is required to remove the first bromine atom.

ALCOHOLS

Bielecki and Henri⁷³ found the absorption of ethyl alcohol to begin at about 2500A.

Several new methods for the purification of alcohol for use as a solvent in absorption spectroscopy were tested by Leighton, Crary and Schipp.⁷⁴ They found the threshold absorption furthest in the ultraviolet for samples which had been allowed to stand for one week over active aluminum amalgam, filtered and distilled. Their results were in general confirmed by Harris,⁷⁵ who preferred, however, to modify the method of preparation introduced by Castille and Henri⁷⁶ by carrying out the final distillation with the aid of zinc wool rather than zinc powder.

Herzberg and Scheibe⁷⁷ found that both methanol and ethanol vapors show

⁶⁷ Muller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **37B**, 365 (1937).

⁶⁸ Müller, E., and Luber, A., *Ber.*, **65B**, 985 (1932).

⁶⁹ Müller, E., and Ehrmann, K., *Ber.*, **69B**, 2207 (1936).

⁷⁰ Aromatic compounds with halogen in the side chain behave similarly, benzyl chloride slowly changing into benzoic acid and $C_6H_5CHCl_2$ yielding benzoyl chloride.

⁷¹ Carrico, J. L., and Dickinson, R. G., *J. Am. Chem. Soc.*, **57**, 1343 (1935).

⁷² Koblitz, W., Meissner, H., and Schumacher, H. J., *Ber.*, **70B**, 1080 (1937).

⁷³ Bielecki, J., and Henri, V., *Ber.*, **45**, 2819 (1912), *Compt. rend.*, **155**, 456 (1912).

⁷⁴ Leighton, P. A., Crary, R. W., and Schipp, L. T., *J. Am. Chem. Soc.*, **53**, 3017 (1931).

⁷⁵ Harris, L., *J. Am. Chem. Soc.*, **55**, 1940 (1933).

⁷⁶ Castille, A., and Henri, V., *Bull. soc. chim. biol.*, **6**, 299 (1924); *Chem. Abs.*, **18**, 3165 (1924).

⁷⁷ Herzberg, G., and Scheibe, G., *Z. physik. Chem.*, **7B**, 390 (1930).

continuous absorption beginning at about 2000Å and extending to 1500Å. They believed a decomposition into alkyl and hydroxyl radicals to be probable. Terenin and Neufmin⁷⁸ find that methanol when decomposed in the Schumann region emits bands indicative of the presence of hydroxyl radicals in excited states. From studies of the continuous absorption of a number of alcohols in the vapor state, Fukumoto⁷⁹ reports the energy of dissociation of the carbon to hydroxyl bond to vary from 133.6 to 152.2 kcal. per mole for the series from methanol to $n\text{-C}_{12}\text{H}_{25}\text{OH}$. For the isomers of butyl alcohol, no regularity was to be found in the energy of this bond, although it was at a maximum, 141.9 kcal., in the normal alcohol.

The alcohols are stable to ultraviolet rays,⁸⁰ unless the wave-lengths be shorter than about 2000Å. Methanol and ethanol are decomposed by such wave-lengths.⁸¹ Methanol gives some formaldehyde, but most is decomposed into hydrogen and carbon monoxide. Indeed, the products of the alcohol⁸² decomposition are said to be about 80 per cent hydrogen and 20 per cent carbon monoxide. (Ethanol gives hydrogen and acetaldehyde.) There is as yet no evidence for the formation of atomic hydrogen. The quantum yield is between one and two.⁸³ From the failure of the para-ortho hydrogen test for free radicals, Patat did not believe the primary process could be the dissociation of the carbon-hydroxyl bond suggested by spectroscopic observations.

Elhart and Orth⁸⁴ state that goldfish are anesthetized more rapidly in methanol or ethanol solutions when these are irradiated because of the formation of aldehyde and acid.

Cantieni⁸⁵ finds that in the presence of oxygen, methanol forms peroxide in the absence of water, the presence of which retards its formation. The peroxide CH_3OOH is assumed to oxidize methanol in the presence of ultraviolet light with the production of traces of formaldehyde. Peroxide formation occurs most rapidly with isalcohols, rapidly with methanol and more slowly in the remaining normal alcohols. In ultraviolet light of longer wave-lengths the rate of formation of peroxides increases with an increase in the number of carbon atoms in the alcohol. Cantieni also finds glycol to form a peroxide $\text{HO-CH}_2\text{CH}_2\text{O}_2\text{H}$. This, reacting with excited glycol molecules, gives carbon dioxide, water and glycol.⁸⁶

According to Henri and Ranc,⁸⁷ glycerol, as such or better in aqueous solutions, suffered some decomposition, especially in the presence of air. A small quantity of a substance giving a positive phloroglucinol reaction for glyceric aldehyde was formed. In alkaline solution, β -acrose was apparently identified by means of the phenyllosazone. Its amount could possibly be increased by the

⁷⁸ Terenin, A., and Neufmin, H., *Nature*, **134**, 255 (1934); *J. Chem. Physics*, **3**, 436 (1935).

⁷⁹ Fukumoto, Y., *Nature*, **134**, 538 (1934).

⁸⁰ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68 (1913); Volmar, *Compt. rend.*, **182**, 1607 (1926).

⁸¹ Patat, F., *Anz. Akad. Wiss. Wien. Math-naturw. Kl.*, **93** (1933); *Chem. Abs.*, **28**, 6371 (1934); Patat, F., and Hoch, H., *Z. Elektrochem.*, **41**, 494 (1935).

⁸² Fricke, H., and Hart, E. J., *J. Chem. Physics*, **4**, 418 (1936) believe methanol to give directly hydrogen and formaldehyde.

⁸³ 0.8 for ethanol in solution, according to Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc.*, **59**, 2450 (1937). Isopropyl alcohol yields acetone and hydrogen. One of the hydrogen atoms comes from the OH and the other from C—H.

⁸⁴ Elhart, W., and Orth, O. S., *Anesthesia and Analgesia*, **14**, 15 (1935); *Chem. Abs.*, **29**, 3401 (1935).

⁸⁵ Cantieni, R., *Ber.*, **69B**, 1101, 1386 (1936). Cf. Milas, N., U. S. P. 2,115,206-7, April 26, 1938, *Chem. Abs.*, **32**, 4606 (1938).

⁸⁶ Cantieni, R., *Z. wiss. Phot.*, **36**, 116 (1937).

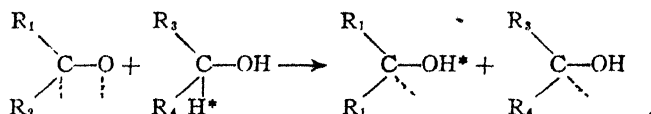
⁸⁷ Henri, V., and Ranc, A., *Compt. rend.*, **154**, 1261 (1912); Bierry, H., Henri, V., and Ranc, A., *Ibid.*, **152**, 535 (1911).

addition of salts of iron, cobalt or uranium before the irradiation. Formaldehyde and acids were also formed.⁸⁸ Cantieni⁸⁹ finds glycerol irradiated in solutions of various concentrations, to give carbon dioxide and water, a peroxide, $\text{OH}\cdot\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OOH}$ being postulated as an intermediate product. The evidence for the formation of the intermediate in this and other alcohol oxidations consisted in a titanium sulfate titration.

The oxidation of ethyl alcohol can be photosensitized by the addition of hydrogen peroxide. The oxidation is a chain reaction of short chain length, compatible with that of the chains postulated in the Haber-Willstätter mechanism of the chain reactions set up in the enzymatic oxidation of alcohol.⁹⁰

The hydrogen peroxide-sensitized oxidation of mannitol known to Henri and Ranc, (l.c.) has recently been studied by Salley.⁹¹ At a constant initial hydrogen peroxide concentration, increase in the mannitol concentration causes an increase in the rate of absorption of oxygen and a simultaneous decrease in the rate of decomposition of the hydrogen peroxide. At a sufficiently high mannitol concentration, however, the rates of both reactions become independent of the mannitol concentration. Since a maximum of two molecules of oxygen can be absorbed for each molecule of hydrogen peroxide which disappears, the photosensitized oxidation of the mannitol does not appear to be a chain process. In the presence of ethylamine, an inhibitor of the photolysis of hydrogen peroxide, the rate of the decomposition of the peroxide in the mannitol mixture is increased. At the same time, the rate of absorption of oxygen apparently decreases, probably owing to the destruction of the hydrogen peroxide with some evolution of oxygen.

Ketones and alcohols undergo mutual oxidation in light, according to Weizmann, Bergmann and Hirschberg,⁹² who cite the earlier observations. Acetophenone and butanol give the pinacol of acetophenone, butanol being dehydrogenated to butyraldehyde. Acetophenone reacts in an analogous fashion with cyclohexanol, phenylmethylcarbinol, ethanol and isopropanol. The system cyclohexanone-cyclohexanol gives but a poor yield of cyclohexanone pinacol. The system acetone-butanol gave two isomeric forms of *sym*-dipropylglycol, and, in the first fractions of the reaction product, butyraldehyde and isopropanol. It is assumed that the first step in these processes is the activation of the carbonyl compound leading to a diradical form which reacts with the carbinol, splitting the C—H bond and giving two radicals. These subsequently stabilize by symmetrical or unsymmetrical dimerization or by a second oxidation-reduction process.



A photocatalytic influence of ketones on the velocity of oxidation of ethyl and other alcohols was described by Cohen.⁹³ The velocity was found to be inde-

⁸⁸ Henri, V., and Ranc, A., *Compt. rend.*, **151**, 316 (1910); *Biochem. Z.*, **64**, 257 (1914).

⁸⁹ Cantieni, R., *Ber.*, **69B**, 1796 (1936).

⁹⁰ Taylor, H. S., and Gould, A. J., *J. Am. Chem. Soc.*, **55**, 859 (1933); *J. Phys. Chem.*, **37**, 367 (1933).

⁹¹ Salley, D. J., *J. Phys. Chem.*, **38**, 465 (1934).

⁹² Weizmann, C., Bergmann, E., and Hirschberg, Y., *J. Am. Chem. Soc.*, **60**, 1530 (1938).

⁹³ Cohen, W. D., *Proc. Acad. Sci. Amsterdam*, **26**, 443 (1923); *Chem. Abs.*, **14**, 2785 (1920); **15**, 3617 (1921); **18**, 50 (1924); Boeseken, J., *Rec. trav. Chim.*, **40**, 433 (1921); **39**, 243 (1920). See also Chapter 25.

pendent of the concentration of the ketone within wide limits and proportional to the alcohol concentration.⁹⁴ The ketone itself either remains unchanged or forms a pinacone. Either benzophenone, aliphatic α -diketones or α , β -diketones with an aromatic nucleus could be employed. No absorption peak in the ketone spectrum appeared to coincide with the wave-length range which proved active (4000-4100A).

Boeseken and Langedijk employed the reaction to effect a partial asymmetric synthesis. The *l*-menthyl ester of *o*-PhCOC₆H₄COOH was used to catalyze the oxidation of racemic methylethylcarbinol and caused after a hundred hours a levorotation of between 0.03 and 0.04° in a 20-cm. tube.

Berthoud⁹⁵ concluded that, at least in the case of benzophenone, it is the ultraviolet absorbed by the ketone which is active. He also found the rate proportional to the intensity of the ultraviolet rather than, as the earlier workers believed, to the square of the visible light intensity. For complete absorption of the available light, the rate, after an induction period of 30 to 60 minutes, reached a steady value inversely proportional to the concentration of oxygen. At 3660A, the quantum yield for oxygen consumed was 18 and the temperature coefficient was 1.7.

Benzoquinone also effects the oxidation of alcohols when irradiated by the wave-lengths 4050, 4080 or 4360A; the quantum yields are unity.⁹⁶

The action of sunlight on the oxidation of alcohols by powdered potassium dichromate⁹⁷ produces only aldehydes. With methyl alcohol, the dichromate is reduced to chromic hydroxide and with ethyl alcohol to a brown powder of unknown composition. The ratio of the yield of aldehyde to the quantity of dichromate reduced increases with the time of exposure and reaches after 12 to 24 hours a value of two. With large quantities of dichromate present, the yield of aldehyde drops because of the screening effect of the precipitates formed and of the dichromate itself. Plotnikow,⁹⁸ as well as Bowen and co workers,⁹⁹ used the dichromate ion in solution. Plotnikow described a wide variety of photo-oxidations effected by this compound. Ethylene glycol rapidly becomes alkaline and deep green, glycolaldehyde and glyoxal being produced. Glycerol solutions yield glyceric aldehyde and acid and dihydroxyacetone. Propyl alcohol gives propionaldehyde and traces of propionic acid, and isopropyl alcohol acetone and acetic and formic acids. Amyl alcohol yields an aldehyde and a brown precipitate of a chromium chromate.

Bowen emphasized the fact that, although in acid solutions the aldehyde is formed without the production of any chromium precipitate, in neutral solutions there results a precipitate of uncertain composition. In neutral and alkaline solutions, the chromate ion present is photochemically inactive. The quantum efficiency is independent of the light intensity, of added acid (if not too little is present), of temperature and of the dichromate ion concentration between 0.1 and 0.01N. Only the ion HCrO₄⁻ is effective. In strongly alcoholic solutions the quantum yield is approximately one, but in weaker solutions it is diminished.

⁹⁴ Boeseken, J., and Langedijk, S. L., *Proc. Acad. Sci. Amsterdam*, **35**, 1124 (1926); Boeseken, J., Cohen, W. D., and Langedijk, S. L., *Rec. trav. Chim.*, **46**, 383 (1927).

⁹⁵ Berthoud, A., *Helv. Chim. Acta*, **16**, 592 (1933).

⁹⁶ Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 694 (1934), see also work of Leighton and Forbes discussed under actinometers in Chapter 7.

⁹⁷ Schwarz, M., *Z. Elektrochem.*, **32**, 15 (1926).

⁹⁸ Plotnikow, J., *Chem. Ztg.*, **52**, 669 (1928); Cantieni, R., *Ber.*, **69B**, 2282 (1936) believes the reaction proceeds through a peroxide.

⁹⁹ Bowen, E. J., and Bunn, C. W., *J. Chem. Soc.*, 2353 (1927); Bowen, E. J., and Yarnold, E. T., *Ibid.*, 1648 (1929); Bowen, E. J., Peacocke, T. A., and Wellburn, E. R., *Ibid.*, 1866 (1931); Bowen, E. J., and Chatwin, J. E., *Ibid.*, 2081 (1932).

With increasing hydrogen ion concentration, the yield increases to a limit of 1.8 or wave-lengths between 4360 and 3665Å.¹⁰⁰

Potassium ferrocyanide solution gives an orange coloration with isobutyl alcohol, especially in light.¹⁰¹

ETHERS

It has been noted¹⁰² that some samples of commercial ether develop peroxides when exposed to ultraviolet rays and so are unsuitable for use in the tropics, although they satisfy all the usual tests for purity. Irradiation may be employed in testing the stability of various samples. Although Athias¹⁰³ believes atmospheric oxygen to be concerned in the decomposition of ether in light, Binz¹⁰⁴ found the photochemical formation of peroxides to be independent of the presence of atmospheric oxygen. Little is known of the nature of the reaction.

In the presence of uranyl nitrate, sunlight is capable of forming oxalic acid from ether, according to Rowell and Russell.¹⁰⁵ They suggest that the light reduces the uranyl to the uranous ion and oxidizes the ether to diglycol, of which part is oxidized to diglycollic acid and part hydrolyzed to glycol, which is further oxidized to oxalic acid.

Milas¹⁰⁶ found the rate of peroxide formation in ethers to depend largely on the type of groups attached to the oxygen atom. Ultraviolet light greatly accelerated the rate of autoxidation of dibenzyl ether in particular.

Acetone photosensitizes dimethyl ether vapor, the rate of decomposition varying with the concentration of the ether, the square root of the absorbed light and inversely as the square root of the acetone concentration.¹⁰⁷ The quantum yields based on carbon monoxide formed were as low as 5 and as high as 230 depending upon the light intensity and total pressure. With diethyl ether, the quantum yields were one-tenth as great under similar conditions.

¹⁰⁰ See also Fugassi, P., *J. Am. Chem. Soc.*, **59**, 2092 (1937).

¹⁰¹ Kutzligng, A., *Z. anal. Chem.*, **77**, 349 (1929); for the action of quinones on alcohols, see Chapter 25.

¹⁰² Liversedge, S. G., *Analyst*, **59**, 815 (1934); *Brit. Chem. Abs.*, **B**, 173 (1935).

¹⁰³ Athias, F., *Thesis (Algiers)*, 1924; *Chim. et ind.*, **14**, 744 (1925); *Chem. Abs.*, **20**, 478 (1926); Matsumami, S., *J. Pharm. Soc. Japan*, No. 520, 529 (1925); *Chem. Abs.*, **20**, 478 (1926).

¹⁰⁴ Binz, C., *Sudder. Apoth. Ztg.*, **70**, 128 (1930).

¹⁰⁵ Rowell, S. W., and Russell, A. S., *J. Chem. Soc.*, **127**, 2900 (1925).

¹⁰⁶ Milas, N. A., *J. Am. Chem. Soc.*, **53**, 227 (1931).

¹⁰⁷ Leetmakers, J. A., *J. Am. Chem. Soc.*, **56**, 1899 (1934).

Chapter 23

The Behavior of Unsaturated Compounds

The compounds discussed in the preceding chapter have been relatively inert photochemically, reacting (if at all) with low quantum yields, except in the case of sensitized processes or in reactions in which the light is absorbed by some other reactant. It has long been known that in ring compounds the presence of double bonds is usually necessary for marked absorption of the longer ultraviolet wave-lengths. Of the olefinic compounds, ethylene exhibits absorption which begins at 2100A and is nearly complete at 1850-1990A, a region in which ethane exhibits no absorption. The introduction of various substituents in molecules containing a double bond frequently displaces the absorption to longer wave-lengths. Particularly effective is the presence of one or more conjugated double bonds, as Smakula has recently demonstrated.¹

Several possible types of reactions may follow upon the absorption of light by double bonds. Usually only one of the two carbon-to-carbon linkings is broken. Polymerization may result, two or more of the photochemically produced molecules with free valences combining. In an absorbing compound with substituents on each carbon atom adjacent to the double bond, after absorption of energy has broken one linkage, there may be a rotation about the remaining linking so that when molecules suffer a collision the double bond may be reformed with the production of the stereoisomer of the original compound. More rarely, and particularly when the shorter wave-lengths have been absorbed, the energy is transferred within the molecule to alkyl groups, which may be decomposed with evolution of hydrogen and formation of compounds with triple linkages.

SIMPLE DECOMPOSITIONS

Mooney and Ludlam² have shown that ethylene can be decomposed by wave-lengths shorter than 2100A, giving acetylene and hydrogen, together with a small amount of a polymerized product.³ The long wave-length limit of 2110A corresponds with the heat of dissociation of ethylene into acetylene and hydrogen, 135 kcal. According to McDonald and Norrish,⁴ ethylene at low pressures when irradiated in the fluoride region deposits a polymer and forms hydrogen and a condensable gas composed of at least two fractions.

In the presence of excited mercury atoms, ethylene is first slightly decomposed and then the remainder is polymerized.⁵ In the presence of hydrogen, ethane is formed, the rate being proportional to the square root of the hydrogen concentration. Taylor and Hill⁶ agree that saturated hydrocarbons are formed,

¹ Smakula, A., *Angew. Chemie*, **47**, 657 (1934).

² Mooney, R. B., and Ludlam, E. B., *Trans. Faraday Soc.*, **25**, 442 (1929).

³ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 207 (1912); Klever, H. W., and Glaser, F., *Mitt. Chem.-tech. Inst. Tech. Hochschule Karlsruhe*, No. 1, 1 (1922); *Chem. Abs.*, **18**, 1976 (1924).

⁴ McDonald, R. D., and Norrish, R. G. W., *Proc. Roy. Soc.*, **157A**, 480 (1936).

⁵ Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.*, **48**, 389 (1926).

⁶ Taylor, H. S., and Hill, D. G., *J. Am. Chem. Soc.*, **51**, 2922 (1929).

but note that they are subsequently decomposed both by the excited mercury atoms and by atomic hydrogen. Methane is the stable product formed in the gas phase and a liquid polymer C_2H_{2x} is deposited on the walls. Jungers and Taylor⁷ find the mercury-sensitized hydrogenation more rapid in the case of deuterio-ethylene than of ethylene. Methane is formed only in negligible amounts, butane being the important product with small amounts of ethane. At low hydrogen concentrations, a photosensitized polymerization occurs; it is slower in the deuterium compound.

In the presence of oxygen, irradiation of ethylene produces some formic acid.⁸ In general, in ethylenic and acetylenic compounds in the presence of oxygen, the double and triple linkages are ruptured and simple acids are formed. In the presence of ammonia, cyclic compounds are produced. Ethylene, for example, first yields amino-ethylenes; then ring formation takes place with production of compounds of the pyrrolidine and pyridine types, which may be regarded as the mother substances of alkaloids. According to Milas, Kurz and Anslow,⁹ hydrogen peroxide reacts with double-bonded compounds on exposure to ultraviolet light to form glycols, possibly because of a decomposition to two hydroxyl radicals. By this reaction, glycerol, dihydroxybutyric acid, *meso*-tartaric acid and its diethyl ester have been prepared from allyl alcohol, crotonic acid, maleic acid and its diethylester, respectively.

Trichloroethylene undergoes a chlorine-sensitized photo-oxidation at 4360Å to dichloroacetyl chloride. It is a chain reaction (quantum yield 40) of zero order with respect to the trichloroethylene and oxygen. The rate is proportional to the absolute intensity of the light absorbed.¹⁰

Matthews and Elder¹¹ produce compounds of sulfur dioxide and unsaturated hydrocarbons by direct combination by exposing the mixed liquids to sunlight or ultraviolet rays, or in some cases by heating. The examples given are the compounds with pseudo-butylene ($C_4H_8SO_2$)_n, propylene, amylene and ethylene. The butylene product is a horny or glassy, clear white solid, soluble in chloroform or tetrachloroethane and not easily flammable. It can be used for making varnishes, transparent films, etc., and may be mixed with celluloid by first softening both with acetone. It renders the celluloid less flammable. Work on this reaction has been reviewed by Snow and Frey,¹² who find from their own experiments that the reaction occurs in the liquid phase, the effective wave-length range being 3000 to 3800Å. It is catalyzed by oxygen, organic peroxides, hydrogen peroxide, but is inhibited by nitric acid or hydrogen sulfide and is slowed at high temperatures.

Uranium salts sensitize various ethylenic compounds as well as aldehydes to sunlight. Acetylenic compounds react even more readily,¹³ aldehyde and formic acid being produced. Amylene yields amyl alcohol. Cyclohexenes, but not cyclohexanes, behave similarly, but benzene does not react in the absence of a side-chain.

The photochemical reduction of sodium dichromate by ethylene glycol has

⁷ Jungers, J. C., and Taylor, H. S., *J. Chem. Phys.*, **6**, 325 (1938).

⁸ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1327 (1910).

⁹ Milas, N., Kurz, P. F., and Anslow, W. P., *J. Am. Chem. Soc.*, **59**, 543 (1937).

¹⁰ Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **B37**, 365 (1937).

¹¹ Matthews, F. E., and Elder, H. M., *British P.* 11,635, May 11, 1914; *Reports Progress Applied Chem.*, **1**, 192 (1916).

¹² Snow, R. D., and Frey, F. E., *Ind. Eng. Chem.*, **30**, 176 (1938).

¹³ Aloy, J., and Valdiviúé, A., *Bull. soc. chim.*, **37**, 1135 (1925).

been found to be affected by the presence of water.¹⁴ For equal amounts of light, the ratio of the reductions occurring in one hour with water present and with it absent was 59 to 79. Within the range of 0.2 to 0.6 per cent concentrations of the dichromate in the glycol, the amount of decomposition was proportional to the time.

Reactions in which halogens are added at the double bond are considered in Chapter 28.

POLYMERIZATION

Berthelot and Gaudechon¹⁵ observed that ultraviolet rays polymerize ethylene to a liquid having the odor of rancid fat, and boiling below 100°C. According to Taylor and Emeléus,¹⁶ the polymerization of ethylene can be sensitized to the light of the mercury arc by means of ammonia, the rate of the reaction increasing with the ammonia concentration. The formation of saturated hydrocarbons in the reaction system with varied ratios of hydrogen to ethylene is subordinate to the polymerization process. An oil is produced which probably contains the nitrogen of the ammonia decomposed in the process. Emeléus and Taylor¹⁷ found methylamine and ethylamine to induce a similar photopolymerization of ethylene at temperatures above 200°C. Jungers and Taylor¹⁸ find that ethylene cannot be polymerized in quenching the resonance radiation of sodium, possibly because of unfavorable localization of the energy received by the ethylene in the quenching process. It can be induced, however, by the photodecomposition of admixed acetone, due to an effect of radicals from the latter. It is also polymerized by ethyl radicals produced by the mercury-sensitized photodecomposition of ethyl iodide.¹⁹

Commercial gaseous butadiene, containing 30 per cent pseudobutylene, but not the pure bivinyl gas, is polymerized in the light of the quartz lamp to a white solid, insoluble in alcohol, ether or benzene.²⁰ Khokhlovkin²¹ found a sample of butadiene completely autopolymerized in light (shorter than 2300 Å) and air at room temperature in 515 days. At 45°C., it occurred in 100 hours. Light considerably increased the rate of the autocatalytic process. Gee²² finds the quantum yield (0.3) of a mercury-sensitized polymerization nearly independent of the pressure. The main product was an insoluble polymer, with some hydrogen and a cyclic dimer, the latter occurring in greatest proportion at low pressures. 2-Butoxy-1,3-butadiene in ultraviolet light for one week gives 13 per cent of a polymer which is somewhat sticky and elastic.²³

Ferrer²⁴ reports that diphenylene ethylene, $(C_6H_4)_2C:CH_2$, is stable for several hours in the dark, but is completely polymerized and rendered insoluble in ether, when exposed for ten minutes to the mercury arc.

¹⁴ Riesenfeld, E. H., and Hecht, O., *Z. wiss. Phot.*, **26**, 369 (1929); *Brit. Chem. Abs.*, **1929A**, 895.

¹⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910).

¹⁶ Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **52**, 2150 (1930); **53**, 573 (1931).

¹⁷ Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 3370 (1931).

¹⁸ Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **4**, 94 (1936); *Chem. Abs.*, **30**, 2109 (1936); *Trans. Faraday Soc.*, **33**, 1353 (1937); *Brit. Chem. Abs. A*, 574 (1937).

¹⁹ Joris, G. G., and Jungers, J. C., *Bull. soc. chim. Belg.*, **32**, 4426 (1938); *Chem. Abs.*, **32**, 4426 (1938).

²⁰ Nikiforov, V. K., and Runtzo, P. M., *Acta Physicochim. U.R.S.S.*, **3**, 335 (1935); *Chem. Abs.*, **30**, 2493 (1936).

²¹ Khokhlovkin, M. A., *Sintet Kauchuk*, No. 4, 12 (1936); *Chem. Abs.*, **30**, 6602 (1936); see also Kublitskii, A. M., *Sintet Kauchuk (U.S.S.R.)*, No. 7-8, 30, 1936; *Chem. Abs.*, **31**, 6503 (1937).

²² Gee, G., *Trans. Faraday Soc.*, **34**, 712 (1938).

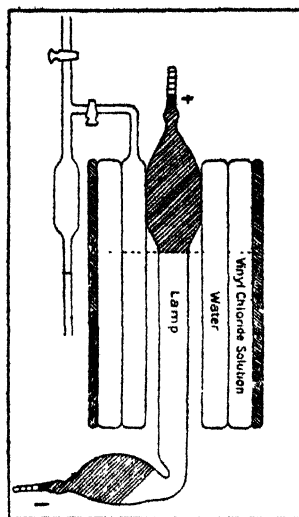
²³ Dykstra, H. B., *J. Am. Chem. Soc.*, **57**, 2255 (1935).

²⁴ Ferrer, J., *Anales soc. espan. fis. quim.*, **20**, 459 (1922); *Chem. Abs.*, **17**, 3177 (1923).

Vinyl chloride and vinyl bromide polymerize rapidly when exposed to light. The chloride forms an amorphous insoluble substance of specific gravity 1.406, which melts above 130°C., with decomposition.²⁵ The polymerized bromide is likewise insoluble in water, alcohol, or ether, has a specific gravity of 2.075 and begins to decompose at 125 to 130°C. Plotnikow²⁶ stated the properties of the vinyl chloride polymer, probably $(\text{CH}_2\text{CHCl})_{10}$, formed by the extreme ultra-violet rays of a mercury arc, to be those of a "synthetic rubber." Sunlight is effective only in the presence of catalysts, such as the salts of manganese, cobalt, nickel, copper and vanadium and most especially, the uranyl salts. A 2.5-per cent solution of vinyl chloride in methyl alcohol was employed in the apparatus shown in Figure 115. Carbon tetrachloride accelerated the transformation. The white precipitate obtained dissolves in many organic solvents to form colloidal systems varying from paste to solid.

FIGURE 115.

Apparatus for Synthesizing "Rubber" from Vinyl Chloride. A water-cooled jacket prevents overheating of the vinyl chloride solution.



Courtesy "India Rubber World"

Ostromuiskenski²⁷ obtained by the polymerization of vinyl bromide a material which he termed caouprene bromide. This exists in three forms, called α , β and γ . When the α and β forms are submitted to the action of ultraviolet the γ form is yielded.

It is claimed²⁸ that if the polymerization of vinyl chloride by sunlight or ultraviolet rays, with or without a catalyst such as a soluble lead salt, is continued beyond the acetone-soluble or α -stage, a new β -modification, insoluble in acetone but soluble in monochlorobenzene, is obtained before conversion into the γ - or δ -forms. The new form may also be obtained from the γ and δ forms by heating them with aniline, quinoline, etc. Monochlorobenzene solutions of the new product to which is added a plasticizer, *e.g.*, a dichlorobenzene, yield flexible, transparent and non-flammable films on drying. The β -product is also obtainable

²⁵ Baumann, E., *Annalen*, 163, 317 (1872).

²⁶ Plotnikow, J., *Z. wiss. Phot.*, 21, 117 (1922); *Chem. Abs.*, 16, 1337 (1922).

²⁷ Ostromuiskenski, L., *J. Russ. Phys. Chem. Soc.*, 44, 204 (1912).

²⁸ Van Dyk, L. A., *British P.* 255,837, June 29, 1926; *Brit. Chem. Abs.*, 1927B, 564.

from the α -compound by prolonged action of ultraviolet rays and heat or by heat alone.²⁹

A vinyl halide may also be condensed with a phenol in the presence of aluminum or ferric chloride, before polymerization by ultraviolet light.³⁰

According to Guyer and Schütze,³¹ 0.1 per cent of hydroquinone prevents the polymerization of vinyl bromide in direct sunlight for several months.

Stobbe and Toepfer³² report that *p*-vinylanisole is polymerized when placed in glass tubes in direct sunlight, the extent of reaction being about the same after four days' exposure as after four hours at 100°C. in the dark. If a little of the polymeric form is added, the polymerization proceeds as far in one day as it does in four with the pure substance. When *p*-vinylanisole in quartz tubes at 30°C. is alternately irradiated by a quartz mercury lamp and kept dark, polymerization appears not to proceed during the period of raying, but during the following periods of darkness. It is believed that polymerization by rays of wave-lengths longer than 3300Å may be reversed by rays of shorter wave-length.

The polymerization of vinyl esters gives rise to various useful products.³³ It may be accelerated by benzoyl peroxide, ozonides, and by anhydrides of organic acids used in conjunction with agents yielding oxygen, as perborates, percarbonates, silver oxide, etc. The polymerization products are solid, colorless and transparent celluloid-like masses which are odorless and can be turned, cut, planed and otherwise manipulated to form various articles. These solids, rendered plastic in hot water, can be molded; upon cooling, the material hardens again. Chlorinated esters may also be polymerized by heat and light in a two-stage operation and employed in lacquers.

Oxygen inhibits the photopolymerization of vinyl acetate, the temperature coefficient of which is markedly greater than unity. The quantum yield is 1.7 at 2300Å, 1.2 at 2536Å and 936 with a 3000 to 4000Å band, indicating a chain mechanism.³⁴ The effects of various inhibitors in ethyl acetate as solvent have been studied by Jeu and Alyea,³⁵ who followed the rate of the reaction by measuring the unsaturation by means of Wijs' solution. Among sixteen representative inhibitors, which include alcohols, esters, acids, amines, oximes, phenols, aldehydes and alkaloids, the relative inhibitory power is approximately the same for this reaction as for the oxidation of sodium sulfite. There is, however, no obvious relation to their effects on the photolysis of hydrogen peroxide. Pyrogallol is about 3200 times as effective an inhibitor as is ethyl alcohol.

Groff³⁶ described a highly plastic composition formed by fluxing on hot differential rolls (100-120°C.) and sheeting out, a mixture of 100 parts vinyl resin (formed by polymerization of 80 parts vinyl chloride and 20 parts vinyl acetate), 60 parts ethylene glycol monoethyl ether diester of ethylene glycol phthalate, 1 part carnauba wax, 1 part calcium stearate and 1 part calcium hydroxide. Exposure for 100 hours to radiation from a mercury arc at a distance of 20 inches caused only a slight discoloration and did not affect the flexibility.

Vinylethynylcarbinols may be polymerized by the action of air, light or both;

²⁹ Van Dyk, L. A., British P. 260,550, July 26, 1926, *Brit. Chem. Abs.* 1927B, 564.

³⁰ British Celanese, Ltd., British P. 409,132, April 18, 1933; *Brit. Chem. Abs.* B, 534 (1934).

³¹ Guyer, A., and Schütze, H., *Helv. Chim. Acta*, 17, 1544 (1934).

³² Stobbe, H., and Toepfer, K., *Ber.*, 57B, 484 (1924); *Chem. Abs.*, 18, 2503 (1924).

³³ Klatte, F., and Rollett, A., U. S. P. 1,241,738, Oct. 2, 1917; cf. Kuhl, H., *Reports of the Progress of Applied Chemistry, Soc. Chem. Ind.*, 1, 192 (1916); *J. Soc. Chem. Ind.*, 34, 623 (1915).

³⁴ Vernon, A. A., and Taylor, H. S., *J. Am. Chem. Soc.*, 53, 2537 (1931).

³⁵ Jeu, K.-K., and Alyea, H. N., *J. Am. Chem. Soc.*, 55, 575 (1933).

³⁶ Groff, F., U. S. P. 1,966,856, July 17, 1934, to Carbide and Carbon Chemicals Corp.

the process is accelerated by the use of halides such as those of zinc, iron, aluminum, antimony, bismuth, boron and tin, organic peroxides such as benzoyl peroxides or acetyl peroxide, ozone, hydrogen peroxide or persalts, or by accelerators of the photochemical reaction such as uranyl nitrate.³⁷ Products of various consistencies and solubilities are obtained, suitable for use in coating compositions, manufacture of safety glass, impregnation of paper or cloth, or in compositions for molding, etc.

Dreyfus³⁸ describes the polymerization of vinyl compounds containing hydrophile groups, as hydroxyl, carboxyl, sulfonic acid, amino or other acid or basic groups, which render them more readily soluble or dispersible in aqueous liquids. Vinyl chloride is heated to 80° to 100°C. in an autoclave with sodium glycol to produce glycolmonovinyl ether; this product may be polymerized by warming with benzoyl peroxide and under the radiation from a quartz mercury-vapor lamp. The polymerized product may be dissolved in water and used directly as a size.³⁹

The polymerization of vinyl chloride by heating with a small proportion of benzoyl peroxide at about 50° to 60°C. for 24 hours may be assisted by a preliminary exposure of the initial material in the gaseous state to rays from a mercury lamp.⁴⁰ Voss and Dickhäuser⁴¹ obtain products resembling celluloid by gradually heating a vinyl halide under pressure to a temperature preferably not above 100°C. The halide may be irradiated, and an inert or a polymerizable organic solvent, such as benzene or butadiene, and a catalyst such as benzoyl peroxide may be present.⁴²

Shmidt states that the powdery product obtained by polymerization of vinyl chloride without a solvent is converted into a colorless, glass-like mass on prolonged exposure to the light of a quartz mercury arc.⁴³

The polymerization of vinyl derivatives of phenols or cresols may be conducted in the presence of anhydrous aluminum chloride or ferric chloride as condensing agents by the action of ultraviolet light or heat.⁴⁴ Pressure polymerization is used in the preparation of resins from vinyl chloride by Waterman, Leendertse and Colthoff.⁴⁵ Although polyvinyl chloride has poor light stability,⁴⁶ glass laminated with a vinyl resin showed no discoloration after exposure for a thousand hours to the Uviarc or after two years in Florida.⁴⁷

³⁷ Carothers, W. H., Berchet, G. J., and Jacobson, R. A., U. S. P. 1,963,074, June 19, 1934, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, **28**, 4848 (1934).

³⁸ Dreyfus, H., British P. 398,173, Sept. 1, 1933; *Chem. Abs.*, **28**, 1360 (1934).

³⁹ Note also Zhukov, I., Komarov, V. A., and Sibiryakova, G. N., *Colloid J. (U.S.S.R.)*, **1**, 9 (1935) for bivinyl polymers. For the effects of light on the oxidation rates of 1,1,5,5-tetraphenyl-1,4-pentadiene and 1,1,6,6-tetraphenyl-1,5-hexadiene, see Bauer, K. H., and Herzog, H., *J. prakt. Chem.*, **147**, 4 (1936).

⁴⁰ Klatte, F., and Müller, H., U. S. P. 1,920,403, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4816 (1933).

⁴¹ Voss, A., and Dickhäuser, E., German P. 579,048, June 20, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4943 (1933); see also British P. 294,474, July 23, 1927, in which vinyl esters are polymerized under ultraviolet to make rubber substitutes, proteins, peptones or amino-acids being added to impart elasticity.

⁴² British P. 385,004, Dec. 22, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4251 (1933).

⁴³ Shmidt, Y., *Org. Chem. Ind. (U.S.S.R.)*, **5**, 116 (1938); *Chem. Abs.*, **32**, 5957 (1938).

⁴⁴ British P. 409,132, April 26, 1934, to British Celanese, Ltd.; *Chem. Abs.*, **28**, 6158 (1934).

⁴⁵ Waterman, H. I., Leendertse, J. J., and Colthoff, P. J. G., *Chem. Weekblad*, **32**, 550 (1935); *Chem. Abs.*, **30**, 1147 (1936); Blackie, K. G., and Crozier, R. N., *Ind. Eng. Chem.*, **28**, 1155 (1936). See also Plauson, H., U. S. P. 2,127,135, Aug. 16, 1938; *Chem. Abs.*, **32**, 8043 (1938) for vinyl acetate polymerization by light when emulsified with sulfonated castor oil.

⁴⁶ Curme, G. O., Jr., and Douglas, S. D., *Ind. Eng. Chem.*, **28**, 1123 (1936).

⁴⁷ Sherts, J. H., and Fix, E. L., *Chem. Met. Eng.*, **43**, 177 (1936). Of a series of synthetic plastics tested for suitability for flexible windshield material for aircraft, cellulose acetobutyrate and vinyl acetate resins showed the greatest resistance to discoloration by ultraviolet light, but had certain disadvantages. Axilrod, B. M., and Kline, G. M., *J. Res. Bureau of Standards*, **19**, 367 (1937).

⁴⁸ Duggan, F. W., U. S. P. 2,126,179, Aug. 9, 1938; *Chem. Abs.*, **32**, 7610 (1938).

For stabilizing vinyl resins to light, Duggan uses one to five per cent of butyl salicylate or other phenol derivative with a single hydroxyl group and an alkyl-substituted carboxyl group ortho to the hydroxyl group.⁴⁸

STEREoisomERIC TRANSFORMATION

The *trans*-isomer has a greater ultraviolet absorption than the *cis*-form in many compounds, including: $\text{ClCH}=\text{CHCl}$, $\text{C}_2\text{H}_5\text{CH}=\text{CHBr}$, $\text{CH}_3\text{CH}=\text{CHBr}$, $\text{ClCH}=\text{CHI}$, and fumaric acid.⁴⁹

The difference between the absorption curves of the geometrical isomers increases with decreasing wave-length. Compounds containing iodine differ in that this relation is inverted at wave-lengths greater than 3000Å, the *cis* form absorbing more in this region than the *trans* form. The inversion may be due in some manner to the liberation of free iodine.⁵⁰

According to van de Walle and Henne,⁵¹ if either the *cis* or *trans* isomer of chloriodoethylene is exposed to sunlight for one hour, the same equilibrium mixture (which contains 17.5 per cent of the *trans* form) is obtained. The theory underlying the conversion of geometrical isomers has been discussed by Olson⁵² and by Mulliken,⁵³ and studies of the process were made in aqueous solutions of various fumaric and maleic acids by Olson and Hudson,⁵⁴ who reviewed the earlier experimental work. It is suggested that in the normal state the carbon atoms of the unsaturated compounds are to be regarded as two tetrahedra joined along a common edge. On excitation by light, they may be considered as joined only at one corner. Rotation about this corner with inversion of one of the carbon atoms will account for the occurrence of a transition between optical isomers if it occurs before a collision removes the energy of excitation and restores a normal state in which the double bond is present. Besides the theory of free rotation in the upper electronic state, Olson discussed the possibility of the addition of an atom or free radical to the face of the carbon tetrahedron, followed by the simultaneous ejection of another group accompanied by isomerization.⁵⁵

The probability p that a molecule in an excited electronic state will return to the *trans* state on deactivation bears to the probability that it will yield the *cis* form ($1-p$) the ratio given by

$$\frac{p}{1-p} = \frac{C_{\text{Tr}}}{C_{\text{Clis}}} \times \frac{\epsilon_{\text{Tr}}}{\epsilon_{\text{Clis}}}$$

in which ϵ_{Tr} and ϵ_{Clis} are the extinction coefficients for the monochromatic light employed and C_{Tr} and C_{Clis} are the mole percentages of the *trans* and *cis* isomers. It was possible to test the relation in the gas state in the case of the isomers of dichloroethylene and dibromoethylene. Agreement with the theory was attained for the stationary states set up at various temperatures, the proportion of the two isomers present being determined by dielectric constant measurements. Further

⁴⁸ Errera, J., and Henri, V., *Compt. rend.*, **180**, 2049 (1925); **181**, 548 (1925). Errera, J., *J. phys. Radium*, **7**, 215 (1926).

⁴⁹ See also Kirmann, A., and Volkringer, H., *Compt. rend.*, **182**, 1468 (1926); Ramart-Lucas, Mme., *Compt. rend.*, **188**, 638, 1301; **189**, 802 (1929); *Bull. soc. chim.*, **51**, 965 (1932); Bourguet, M., Gredy, B., and Piaux, L., *Compt. rend.*, **195**, 129 (1932).

⁵¹ Van de Walle, H., and Henne, A., *Bull. sci. acad. roy. Belg.*, **11**, 360 (1925); *Chem. Abs.*, **20**, 1049 (1926).

⁵² Olson, A. R., *Trans. Faraday Soc.*, **27**, 69 (1931).

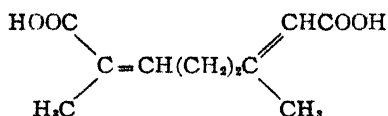
⁵³ Mulliken, R. S., *Phys. Rev.*, **41**, 751 (1932).

⁵⁴ Olson, A. R., and Hudson, F. L., *J. Am. Chem. Soc.*, **55**, 1410 (1933).

⁵⁵ Olson, A. R., *J. Chem. Physics*, **1**, 418 (1933).

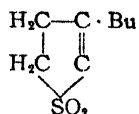
studies in the case of the chlorine compounds have been reported by Mahncke and Noyes.⁵⁸ There are three absorption regions: (1) continuous, by the carbon-chlorine bond from about 2500Å with maxima at 1950Å for the *cis* and 1850Å for the *trans* form; (2) bands beginning at about 1540Å, and (3) another continuous region extending down to 750Å. In the first absorption region, produced by irradiation with an aluminum spark, atomic chlorine appears to be formed, with possibly some hydrogen chloride. For this reason, Olson's second theory is favored when the change is induced by light in this region of the spectrum. *cis*-Dichloroethylene also yields small amounts of a solid polymerization product, melting at 103.5° to 104°C. These observations have also been confirmed by Müller and Ehrmann.⁵⁷

The compound



undergoes a *cis-trans* isomerization in ultraviolet light to a more soluble form.⁵⁸

Other Types of Isomerization. The isomerization of the sulfones of β -alkylbutadienes in alkaline solution under the influence of ultraviolet light consists in a displacement of the double linking in the ring toward the alkyl.⁵⁹ *Tert*-butylbutadienesulfone is isomerized to a compound



The isomer of the sulfone of 2-phenyl-1,3-butadiene and ozone when irradiated gave propiophenonesulfonic acid, showing that the change was not a *cis-trans* isomerism, as believed by Eigenberger⁶⁰ to occur in the irradiation of isoprene sulfone in the presence of alkali.

The homologs of isoprenesulfone isomerize on exposure to ultraviolet,⁶¹ the change involving a wandering of the double bond.

According to Sherrill, Otto and Pickett,⁶² sunlight and ultraviolet light of shorter wave-lengths transform 2-pentene into an isomeric form with slightly different physical properties. The transformed product adds hydrogen bromide to form 15 per cent of 3-bromopentane and 85 per cent of 2-bromopentane.⁶³ Birch and Stansfield⁶⁴ note that ultraviolet light favors the formation of a peroxide in cyclohexene.

⁵⁸ Mahncke, H. E., and Noyes, W. A., Jr., *J. Chem. Physics*, **3**, 536 (1935); *J. Am. Chem. Soc.*, **58**, 932 (1936).

⁵⁷ Müller, E., and Ehrmann, K., *Ber.*, **69B**, 2207 (1936). See also Stockmann, H., and Stoermer, R., [*Ber.*, **47**, 1793 (1914)] for work on γ -phenylvinylacetic acid in benzene solution.

⁵⁹ Kuhn, R., Köhler, L., and Köhler, F., *Z. physiol. Chem.*, **242**, 171 (1936).

⁶⁰ Backer, H. J., and Strating, J., *Rec. trav. chim.*, **54**, 170, 618 (1935); *Chem. Abs.*, **29**, 2959 (1935); **30**, 3403 (1936).

⁶¹ Eigenberger, E., *J. prakt. Chem.*, **129**, 312 (1931); *Chem. Abs.*, **25**, 2969 (1931); see also van Zuydewijn, E. de R., *Rec. trav. chim.*, **56**, 1047 (1937).

⁶² Backer, H. J., and Strating, J., *Rec. trav. chim.*, **53**, 525 (1934); Backer, H. J., Strating, J., and Zuthoff, A. J., *Ibid.*, **55**, 761 (1936).

⁶³ Sherrill, M. L., Otto, B., and Pickett, L. W., *J. Am. Chem. Soc.*, **51**, 3032 (1929).

⁶⁴ For the ultraviolet absorption spectra of the various isomeric 2-pentenenes, Carr, E. P., *J. Am. Chem. Soc.*, **51**, 3041 (1929).

⁶⁵ Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

Acetylene. The pure gas exhibits a banded absorption spectrum which begins at 2400A according to Kistiakowsky,⁶⁵ or at 2300A according to Hopfield,⁶⁶ or at lower pressures (less than 30 mm.) at 2070A.⁶⁷ A second system begins at about 1540A and at higher pressures a continuous absorption appears to set in at about 1880A, but may be due to an impurity.⁶⁸ Jonescu gives an extrapolated heat of dissociation of 204 kcal. Kato,⁶⁹ however, claims to have noted on the vaporization of solid acetylene at room temperatures, a broad continuous absorption spectrum and some series of bands with fine structure. The former, showing its strongest absorption at 2560 and 2400A, is held to indicate predissociation. The latter, appearing below 2500A, is attributed to deformation vibrations.

Berthelot and Gaudechon⁷⁰ found exposure of acetylene to the action of ultraviolet rays to bring about a partial polymerization to a yellow solid, but no decomposition. No benzene was found in these experiments.

Daylight or sunlight does not affect carefully purified and dried acetylene, but with wave-lengths less than 3000A, the reaction occurs at atmospheric or higher pressures and at room temperature, giving the yellow product without any separation of carbon.⁷¹ The process is disturbed by the presence of oxygen or moisture, the latter leading to the formation of aldehyde. The wave-length limit was set at 2537A or less by Lind and Livingston,⁷² who found the rate of polymerization to be proportional to the intensity of the absorbed light but independent otherwise of the acetylene pressure. The temperature coefficient was 1.25, and the quantum yield appeared to be 9.2 for the wave-length 2150A. This value was somewhat uncertain since measurements had to be limited to the beginning of the reaction owing to the deposition of the polymer on the walls of the vessel. The solid product, cuprene or a very similar substance, had the empirical formula $(C_{10}H_9)_n$. Some benzene formation was observed and could be accounted for by side reactions. Kato confirmed the formation of both cuprene and benzene by the wave-lengths 2103, 2100.5, 2065, 2036 and 2026A, but believed 2200A to produce chiefly benzene. At higher temperatures, 270° to 376°C., both he and Livingston and Schifflett⁷³ found benzene to predominate; the latter workers observed that two nonvolatile solids and a yellow, viscous, volatile liquid were also produced. By following the absorption changes during the polymerization of acetylene, Kemula and Mrazek⁷⁴ detected the formation not only of benzene, but of naphthalene as well, together with less than 0.25 per cent of ethylene and ethane, but no hydrogen in the gas phase. Bates and Taylor⁷⁵ noted that polymerization could also be effected by excited mercury atoms, but that acetylene could not be hydrogenated by hydrogen which had been activated by excited mercury vapor.

⁶⁵ Kistiakowsky, G. B., *Phys. Rev.*, **37**, 276 (1931).

⁶⁶ Hopfield, J. J., *Phys. Rev.*, **29**, 356 (1927).

⁶⁷ Herzberg, G., *Trans. Faraday Soc.*, **27**, 379 (1931).

⁶⁸ For data on the classification of the bands, see Pice, W. C., *Phys. Rev.*, **45**, 843 (1934); Jonescu, A., *Compt. rend.*, **199**, 710 (1934); Woo, S.-C., Liu, T.-K., Chu, T. C., and Chih, W., *J. Chem. Phys.*, **6**, 240 (1938).

⁶⁹ Kato, S., *Bull. Inst. Phys.-Chem. Research (Tokyo)*, **10**, 343 (1931); *Chem. Abs.*, **25**, 5845 (1935).

⁷⁰ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910); **151**, 395 (1910); **155**, 521 (1912).

⁷¹ Reinicke, H., *Z. angew. Chem.*, **41**, 1144 (1928).

⁷² Lind, S. C., and Livingston, R. J., *Am. Chem. Soc.*, **52**, 4613 (1930); **54**, 94 (1932).

⁷³ Livingston, R., and Schifflett, C. H., *J. Phys. Chem.*, **38**, 377 (1934); see also Ch. Rosenblum, *Bull. soc. chim. Belg.*, **46**, 503 (1937); *Chem. Abs.*, **32**, 2840 (1938).

⁷⁴ Kemula, W., and Mrazek, S., *Z. physik. Chem.*, **23B**, 358 (1933).

⁷⁵ Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **49**, 2438 (1927).

Toul⁷⁶ believed polymerization in the presence of mercury vapor should not be considered a true photosensitization since it can still be observed when a source is used which does not emit the lines which excite mercury. The addition of 0.006 per cent of oxygen did not affect the reaction. He also believed that an equilibrium was reached with the polymer after the volume had been reduced by 10 per cent, but this result could not be duplicated by Kemula.⁷⁷ Melville⁷⁸ treats the process as a sensitized chain reaction in which the excited mercury atoms form with the acetylene molecule a complex which successively builds up. The chain length is independent of the acetylene pressure, or surface, or of the rate at which the chains are started and may at 250°C. attain a maximum of 100. Cessation of growth is attributed to a special type of collision of the growing polymer with an acetylene molecule. Jungers and Taylor⁷⁹ found the rate of this photosensitized reaction to be 30 per cent greater with acetylene than with heavy-hydrogen acetylene. They gave the quantum yield as 6.5 for acetylene and 5 for acetylene-D₂.

Both methylacetylene and its double-bonded isomer allene can also be polymerized to white solids by ultraviolet radiation,⁸⁰ the quantum yields being 3.5 and 2.5, respectively. Diacetylene can also be polymerized.⁸¹

The photochemical oxidation of acetylene yields oxalic acid and a trace of aldehyde.⁸² A mechanism was suggested by Mecke⁸³ according to which an excited acetylene molecule adds directly to an oxygen molecule. Livingston notes that further oxidation of the resulting glyoxal would account for the formation of the oxalic acid. It is also possible that two molecules of oxygen might be added to the excited acetylene molecule, the double peroxide then rearranging to oxalic acid. In the presence of water vapor in the gas phase in the absence of oxygen or in an aqueous solution, Livingston and Schifflett⁸⁴ could detect neither the formation of aldehydes nor ketones.

Heinemann⁸⁵ claims to secure the union of acetylene and methane by heating these gases or irradiating them with ultraviolet rays, in the presence of such catalytic metals as iron, nickel, copper, silver, iridium or platinum.

Carothers⁸⁶ finds the addition of thio-*p*-cresol to divinylacetylene $\text{CH}_2=\text{CH}\equiv\text{CH}=\text{CH}_2$ to be powerfully accelerated by the light of a mercury arc transmitted through soda-glass.

Polymerization of 1-chloro, 1-bromo- and 1-iodo-2-vinylacetylene to form resinous solids may be accelerated by the use of ultraviolet light, benzoyl peroxides, ozonides, etc. The iodine and bromine polymers are very explosive, and the chlorine derivative less so.⁸⁷

Aldehydes and Ketones.⁸⁸ *Absorption.* These compounds in the gaseous

⁷⁶ Toul, F., *Coll. Czech. Chem. Comm.*, **6**, 162 (1934); *Brit. Chem. Abs.*, **A**, 852 (1934).

⁷⁷ Kemula, W., *Coll. Czech. Chem. Comm.*, **7**, 319, 491, 493 (1935); *Chem. Abs.*, **29**, 7775 (1935); **30**, 1644 (1936).

⁷⁸ Melville, H. W., *Trans. Faraday Soc.*, **32**, 258 (1936).

⁷⁹ Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **3**, 338 (1935).

⁸⁰ Lind, S. C., and Livingston, R., *J. Am. Chem. Soc.*, **55**, 1036 (1933).

⁸¹ Müller, F. G., and Banninger, A., *Helv. Chim. Acta*, **10**, 763 (1927).

⁸² Livingston, R., *J. Am. Chem. Soc.*, **53**, 3909 (1931).

⁸³ Mecke, R., *Trans. Faraday Soc.*, **27**, 374 (1931).

⁸⁴ Livingston, R., and Schifflett, C. H., *J. Phys. Chem.*, **36**, 750 (1932).

⁸⁵ Heinemann, A., U. S. P. 1,202,385, Oct. 24, 1916; 1,134,667, Apr. 7, 1915.

⁸⁶ Carothers, W., *J. Am. Chem. Soc.*, **55**, 2008 (1933).

⁸⁷ Jacobson, R. A., U. S. P. 1,967,864, July 24, 1934; *Chem. Abs.*, **28**, 5834 (1934).

⁸⁸ For a recent review, see Leighton, P. A., *J. Phys. Chem.*, **42**, 749 (1938).

state exhibit a broad absorption band attributed to the carbonyl group and having its maximum at about 2900 to 2800A.⁸⁹

In hexane solutions, the absorption is in general similar. Formaldehyde, for example, either as vapor or in hexane at -70° , exhibits absorption chiefly between 3542 and 2750A, the maximum being at 2940A in hexane and at 2935A in the vapor.⁹⁰ Acetaldehyde and propionaldehyde behave similarly. Data on hexane solutions of higher aldehydes through octylaldehyde have been given by Conrad-Billroth.⁹¹

In water, however, the absorption of the three lowest aldehydes is somewhat displaced toward shorter wave-lengths, the maximum being at 2800A. The formation of hydrates also decreases the absorption. Choral hydrate lacks the typical aldehyde absorption band. The same is true of methylal and acetal.⁹² Schou believes that in aqueous formaldehyde solutions there is less than one molecule of formaldehyde for 1200 molecules of the hydrated or polymerized form. Under certain conditions (the presence of a trace of alkali or after polymerization by acid) acetaldehyde gives spectral evidence that some of the molecules are present in enolic form.⁹³ This may be detected by a study of the absorption coefficients near the minimum close to 2400A. Herold and Wolf⁹⁴ find that propionaldehyde in water forms an association complex and a hydrate which do not absorb in the same region as the carbonyl group. In propyl alcohol as solvent, absorption measurements indicate that the greatest part of the aldehyde has been converted to the half-acetal.⁹⁵

Interpretations of the absorption spectra of formaldehyde vapor have been given by Henri and Schou,⁹⁶ by Herzberg,⁹⁷ and by Dieke and Kistiakowsky.⁹⁸

Observations in the far ultraviolet at 1750 to 1150A have been reported by Price.⁹⁹ About 32 bands are distinguished between 3550 and 2500A. Those on the longer wave-length side contain rotational fine structure but become diffuse, indicating predissociation, at about 2670A to 2750A. This limit is shifted toward the red at higher temperatures.

Reactions. Berthelot and Gaudechon¹⁰⁰ showed that ultraviolet light decomposes formaldehyde vapor with the production of carbon monoxide and hydrogen but no carbon dioxide. Some polymerization also occurred. Bredig and von Goldberger, however¹⁰¹ claimed to have detected small amounts of carbon dioxide and methane, but Norrish and Kirkbride¹⁰² were unable to verify these results. They

⁸⁹ Purvis, J. E., and McClelland, N. P., *J. Chem. Soc.*, 103, 433 (1913); Bielecki, J., and Henri, V., *Ber.*, 45, 2819 (1912); Purvis, J. E., *J. Chem. Soc.*, 127, 9 (1925); Eastwood, E., and Snow, C. P., *Nature*, 133, 908 (1934).

⁹⁰ Schou, S. A., *Compt. rend.*, 186, 690 (1928).

⁹¹ Conrad-Billroth, H., *Z. physik. Chem.*, B23, 315 (1933).

⁹² Schou, S. A., *Compt. rend.*, 182, 965 (1926); *I. chim. phys.*, 26, 69 (1929).

⁹³ See also Kwieciński, L., and Marchlewski, L., *Bull. soc. chim.*, 45, 591 (1929).

⁹⁴ Herold, W., and Wolf, K. L., *Z. physik. Chem.*, B12, 165 (1931); *Z. Elektrochem.*, 39, 566 (1933).

⁹⁵ See also Backès, M., *Compt. rend.*, 200, 1669 (1935).

⁹⁶ Henri, V., and Schou, S. A., *Nature*, 118, 225 (1926); *Z. Physik*, 49, 774 (1928); *J. chim. phys.*, 25, 665 (1928); *Compt. rend.*, 182, 1612 (1926); 186, 1050 (1928); 199, 849 (1934).

⁹⁷ Herzberg, G., *Trans. Faraday Soc.*, 27, 378 (1931).

⁹⁸ Dieke, G. H., and Kistiakowsky, G. B., *Phys. Rev.*, 45, 4 (1934); *Proc. Nat. Acad. Sci.*, 18, 367 (1932). See also Kato, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 23, 256 (1934), *Chem. Abs.*, 28, 4312 (1934).

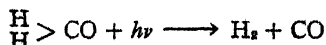
⁹⁹ Price, W. C., *Phys. Rev.*, 46, 529 (1934).

¹⁰⁰ Berthelot, D., and Gaudechon, H., *Compt. rend.*, 151, 478 (1910).

¹⁰¹ Bredig, G., and von Goldberger, A., *Z. physik. Chem.*, 110, 521 (1924); see also Frank, A., and Pollitzer, E., *Monatsh.*, 34, 797 (1913).

¹⁰² Norrish, R. G. W., and Kirkbride, F. W., *J. Chem. Soc.*, 135, 1518 (1932); *Trans. Faraday Soc.*, 27, 404 (1931).

show from the nature of the products and from energetic considerations that, although the light is absorbed by the carbonyl group, the primary dissociation does not yield a CH_2 group and an oxygen atom. Instead, CO is thought to be removed bodily, the hydrogen atoms combining without first separating from the molecule.



This view was based upon what was then known of the behavior of other aldehydes and ketones. If ketones with two different alkyl groups should produce free radicals in the primary process, a mixture of hydrocarbons might be expected as a result of the photochemical decomposition. Actually, it appeared that only one hydrocarbon resulted. Should a free methyl radical be produced from acetaldehyde in the primary process, one might expect ethane as well as methane. This was not observed. Furthermore, a primary process involving free radicals might give rise to a short chain reaction, the free radicals reacting with an additional molecule of the original aldehyde or ketone. Bowen and Watts¹⁰⁰ did, indeed, find a quantum yield of two for the decomposition of acetaldehyde, but it seemed that the occurrence of a complicating polymerization made these results not very accurate. Norrish and Kirkbride therefore proposed as a general mechanism for the primary process in the decomposition of aldehydes and ketones, the elimination of CO, the remaining radicals combining without first separating from the molecule. Subsequent work has shown, however, that other processes must also be admitted. See, for example, the discussion of acetone.

The formaldehyde decomposition can be made to proceed by wave-lengths corresponding to the region of rotational fine structure, that is, by wave-lengths longer than those which cause predissociation. The quantum yield was 1.1 at 3030 to 3130Å or 0.7 at 3340 to 3650Å. In the predissociation region the quantum yield was 0.9 (2540-2650Å).

Later, Patat¹⁰⁴ found that the addition of oxygen produced no change in the ratio of hydrogen to carbon monoxide produced by irradiating formaldehyde vapor within the fine structure region longer than 3000Å and uncomplicated by an underlying continuum. From this it was concluded¹⁰⁵ that no hydrogen atoms are there produced. Patat showed the same to be true of the reaction conducted in part of the predissociation region (3000-2700Å), thus supporting the Norrish mechanism. The presence of free hydrogen atoms could, however, be detected by this method when the irradiation was made in the region of continuous absorption.

The primary process advanced by Mecke¹⁰⁶ and by Herzberg¹⁰⁷ involved a dissociation in the predissociation region into H and HCO. This was assumed to require 92 kcal., the energy of the 2750Å line being 105 kcal. Norrish and Patat each gave reasons for believing that this is not the actual process at the longer-wave portions of the predissociation region. Patat suggests that molecular thermal vibrations may contribute part of the energy required for the simultaneous breaking of two C-H bonds, which must occur since hydrogen atoms are not detected.

Experiments by Norrish and Noyes with radiations in the Schumann region gave no evidence for the formation of oxygen atoms and CH_2 in the primary process, due probably to wave-lengths shorter than 1600Å. The final products were the same as those produced by longer wave-lengths in the near ultraviolet.¹⁰⁸

¹⁰⁰ Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 129, 1607 (1926).

¹⁰⁴ Patat, F., *Z. physik. Chem.*, 25B, 208 (1934).

¹⁰⁵ Patat, F., and Löcker, T., *Z. physik. Chem.*, 27B, 431 (1934).

¹⁰⁶ Mecke, R., *Nature*, 125, 526 (1930).

¹⁰⁷ Herzberg, G., *Trans. Faraday Soc.*, 27, 383 (1931).

¹⁰⁸ Norrish, R. G. W., and Noyes, W. A., Jr., *Proc. Roy. Soc.*, A163, 221 (1937).

Before considering the photolysis of other aldehydes, a few other reactions of formaldehyde may be briefly mentioned. Ghosh and Nandy¹⁰⁹ found its oxidation by hydrogen peroxide in acid solution with a tungstic acid sol as photosensitizer, to be unimolecular with respect to hydrogen peroxide at low concentrations. It tended to become of zero order at higher ones. For low concentrations of free hydrochloric acid, the velocity coefficient varies as the square root of the intensity of the incident radiation, but the variation of the velocity with the intensity of the light is much less at higher acid concentrations. The quantum efficiency of the reaction is between two and seven.

In a reaction between chlorine and formaldehyde, the final products are carbon monoxide and hydrogen chloride. By an analysis of the curves giving the change of pressure with time of irradiation, Krauskopf and Rollefson,¹¹⁰ who used mixtures of the reactants in various proportions, concluded two reactions to be involved. The first, a very rapid reaction, involved the formation of a new intermediate compound, formyl chloride, produced together with hydrogen chloride by the action of chlorine atoms, formed in the primary photochemical process, upon formaldehyde. This then reacted more slowly in a secondary reaction, which might be either a thermal or a sensitized photochemical reaction, to yield carbon monoxide and hydrogen chloride. This decomposition appeared to be a heterogeneous surface reaction. Under certain conditions, the first reaction proceeded with explosive rapidity. The overall reaction had a quantum yield of about 10⁴, and was very susceptible to the action of such inhibitors as oxygen or mercuric chloride. Side reactions, such as the polymerization or decomposition of formaldehyde, the formation of phosgene, or one between hydrogen chloride and formaldehyde, were so slow as to be negligible.

Roman¹¹¹ claims to convert such aldehydes as formaldehyde into alcohols by the action of luminous energy from which harmful radiations have been filtered.

Acetaldehyde. Acetaldehyde is also partly polymerized and partly decomposed into methane and carbon monoxide in ultraviolet light,¹¹² even that of sunlight. In some experiments of Berthelot and Gaudechon particularly with extreme ultraviolet rays, it was observed that the proportion of methane to carbon monoxide was somewhat less than exactly that corresponding to a simple decomposition. This was assumed to be due to a polymerization of the acetaldehyde in part to paraldehyde which was then photolyzed to carbon monoxide and ethane or more complex substances. Radiations of wave-length 2500A caused a rapid polymerization, both paraldehyde and metaldehyde being formed. The presence of water checked these processes, but favored the formation of formic acid. It was also believed that even in the absence of oxygen, a portion of the aldehyde was oxidized to acetic acid.

By comparison with a uranyl oxalate actinometer the quantum yield of which was taken as one, Bowen and Watts¹¹³ concluded that in the unsaturated vapor of acetaldehyde, the quantum yield for polymerization is 1.6 and for decomposition 0.4. The use of the more accurate value of 0.55 for the quantum yield of the actinometer found by Leighton and Forbes¹¹⁴ makes these values 0.88 and 0.22, respectively.

The absorption of acetaldehyde extends from about 3480 to 2300A, with a maximum at about 2890A, the absorption falling off on either side, according to Smith.¹¹⁵ Bands with distinct rotational structure set in faintly at 3484A and extend to about 3300A, below which the structure gradually becomes more diffuse and disappears because of predissociation near 3080A. From this wave-length, however,

¹⁰⁹ Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, **6**, 975 (1929); *Chem. Abs.*, **24**, 2055 (1930).

¹¹⁰ Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2542 (1934).

¹¹¹ Roman, L. H., French P. 734,065, July 19, 1930; *Chem. Abs.*, **27**, 992 (1933).

¹¹² Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68, 233 (1913).

¹¹³ Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (1926).

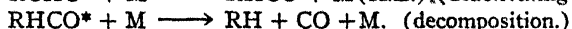
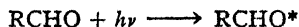
¹¹⁴ Leighton, W., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930).

¹¹⁵ Smith, J. H. C., *Carnegie Inst. Reports*, **27**, 178 (1928).

about 60 diffuse bands continue to 2820Å.¹¹⁶ According to Leighton and Blacet¹¹⁷ these diffuse bands extend even further to 2730Å, and traces can be detected even at 2660Å. There is also, underlying the banded absorption, a broad continuous absorption, which begins at about 3080, that is, in the region where the bands still show some rotational fine structure; it has a maximum at 2750Å. The greatest total absorption (bands plus continuum) occurs at 1890Å.¹¹⁸

Using the total radiation from a mercury arc, Smith¹¹⁹ found the rate of the decomposition of acetaldehyde vapor to be independent of pressure and directly proportional to the intensity of the incident light. That of polymerization was directly proportional to pressure and proportional to the logarithm of the light intensity. Smith found that decomposition is produced chiefly by the shorter wave-lengths, and that polymerization could be produced throughout the absorption band with an estimated quantum yield of only 0.04 for an average wave-length of 2650Å.

Leighton and Blacet in general confirmed the observations of Smith on the relative predominance of the two types of reactions at various wave-length regions by careful studies of the quantum yields of each at several pressures in the fine structure, predissociation and predominantly continuous regions. Fluorescence of the aldehyde vapor could be observed between 3342 and 2804Å, but not at shorter wave-lengths. Because of this, it was suggested that a mechanism involving activated molecules must apply in these regions and be concerned with polymerization. It was found that the yield for the polymerization reaction at a pressure of 200 mm. dropped from 0.47 at 3130Å to only 0.1 at 2537Å in the region of continuous absorption. Conversely, the yields for decomposition were 0.2 and 0.9 under these conditions. At 3130Å there is considerable fluorescence, the bands are not altogether without fine structure and the amount of continuous absorption is small. Here the yield of polymerization increases with the pressure from 0.266 at 14 mm. to 0.638 at 291 mm. The yield for decomposition decreases from 0.396 at 14 mm. to 0.193 at 291 mm. This decrease was attributed to a removal of activated molecules, which were believed also to contribute to the process of dissociation. The mechanism suggested for the observations in this wave-length region were analogous to those of Norrish for the decomposition of formaldehyde in its long wave-length region.



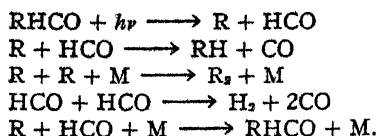
In the region of pure continuous absorption below 2730Å where the quantum yield of decomposition approaches unity, increasing the pressure had almost no effect on the yield. In this region, where there was no fluorescence, as well as in the diffuse predissociation bands, a decomposition mechanism was suggested as had been proposed by Herzberg. It differed from that of Norrish in assuming the presence of free radicals.

¹¹⁶ Schou, S. A., and Henri, V., *Z. Physik*, **49**, 774 (1928); Henri, V., *Trans. Faraday Soc.*, **25**, 765 (1929); Schou, S. A., *J. chim. phys.*, **26**, 1 (1929).

¹¹⁷ Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **55**, 1766 (1933).

¹¹⁸ For the influence of acids and alkalis upon the absorption spectra of aqueous solutions altering the amount of an enolic form, see Schou, S. A., *Compt. rend.*, **184**, 1452 (1927) and Fromageot, C., *J. chim. phys.*, **24**, 623 (1927).

¹¹⁹ Smith, J. H. C., *loc. cit.*



That some polymerization (yield 0.1) could still be observed at these wavelengths suggested the possibility that the free radicals could induce polymerization in other molecules through the formation of intermediate compounds.

Particularly interesting results were obtained with the wave-length 3342Å which lies between two band maxima, so that the absorption is ascribed principally to the weak underlying continuum. The result was a high quantum yield for decomposition as in the short wave-length regions (0.72-0.82) and little or no polymerization. This observation and the gradual changes in the quantum yields of the two processes, with no sharp breaks, agreed with the gradual transition observed between the different absorption regions. The maximum probability of excitation to the upper electronic state which leads to dissociation occurs at about 3100Å, very close to the point at which all rotational structure disappears from the bands.

The chief support advanced for the proposed dissociation mechanism was the subsequent¹²⁰ finding of hydrogen in the decomposition products by a new method of microanalysis,¹²¹ although Leighton and Blacet had been unable to detect it in their original work. From the ratios of hydrogen to carbon monoxide found at three wave-lengths, (0.05 at 3130Å, 0.10 at 2804Å and 0.155 at 2537Å), it was concluded that the fraction of the molecules yielding hydrogen increases linearly from 10 per cent at 3130 to 31 per cent at 2537Å. These observations made at 300 mm. favored a short-chain reaction at room temperatures.

Leermakers¹²² found that at temperatures above 80°C., and with irradiation of acetaldehyde by 3130Å, the short-chain reactions leading to the production of hydrogen were replaced by or accompanied by longer chains leading to the production of methane along with carbon monoxide. The rate of the chain reaction was proportional to the concentration of the aldehyde and to the square root of the light intensity. Below temperatures of 160°C., a term, 0.3 *I*, had to be added to the rate equation to cover that photolysis which was not a part of the chain reaction. The quantum yield increased enormously with the temperature reaching 310 at 309.5°C., when light of low intensity was used. In the case of formaldehyde, Leermakers also found a chain length of 100 at temperatures between 100° and 400°C. On the other hand, the acetone decomposition is not similarly affected, the quantum yield remaining at 0.76 at high temperatures. He suggests that acetone may follow the Norrish type of primary process, although acetaldehyde exhibits a chain mechanism involving methyl radicals. The energy of activation for the reaction: $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$ is 9.8 kcal. and that of the formaldehyde reaction $\text{H} + \text{HCHO} \rightarrow \text{H}_2 + \text{HCO}$ is 16.2 kcal. Patat¹²³ uses the para-hydrogen conversion method for calculating the free radical concentrations. Blacet and Volman now believe the Leermakers chain mechanism for the reaction at high temperature applies also at room temperatures.

¹²⁰ Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58**, 278 (1936); Blacet, F. E., and Volman, D., *Ibid.*, **60**, 1243 (1938).

¹²¹ Blacet, F. E., and MacDonald, G. D., *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934). Compare Franke, A., and Pollitzer, E., *Monatsh.*, **34**, 797 (1913).

¹²² Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1537 (1934)

¹²³ Patat, F., *Naturwiss.*, **24**, 62 (1936); *Z. physik. Chem.*, **32B**, 274 (1936).

Pearson¹²⁴ failed to detect free radicals in the primary products of the photolysis of acetaldehyde and of propionaldehyde (as well as methylbutyl ketone) by their action on metallic mirrors, although they could be detected in the case of acetone, methyl ethyl ketone and diethyl ketone. Later, however, Pearson and Purcell¹²⁵ succeeded in demonstrating the presence of free radicals in the case of acetaldehyde and attributed previous failures to the presence of a thin film of polymerized aldehyde upon the mirrors. Since, when equal quantities of acetaldehyde and acetone were irradiated, six times as many free radicals were found as when the aldehyde alone was used, it was suggested that there may be some underlying difference in the mechanisms of the photolyses of aldehydes and ketones, although it was concluded that free radicals must be admitted, as Leighton and Blacet maintained, to play some part in the photolysis of aldehydes. Glazebrook and Pearson,¹²⁶ who have measured the relative quantities of free radicals formed by the dissociation of a number of ketones, state that in the case of acetone, the acetyl and methyl radicals are formed in comparable quantities. The former, however, rapidly combine with one another to form diacetyl, and have a short life, possibly dissociating further into a methyl radical and carbon monoxide.

It was earlier claimed by Ghosh and Nandy¹²⁷ that the decomposition in dilute aqueous solutions involves a chain reaction, since the quantum yield is 13.4. They found the reaction to be unimolecular, the velocity coefficient being independent of the initial concentration. There was a small but definite temperature coefficient.

Discherl¹²⁸ states that acetoin, $\text{CH}_3\text{CH}(\text{OH})\text{COCH}_3$, is formed when aqueous solutions of acetaldehyde or of pyruvic acid are irradiated by ultraviolet light, but the mechanism is not clear. A quartz apparatus designed for carrying out this reaction has been described by Benson and Cadenhead.¹²⁹

The action of ultraviolet light on trimethylacetaldehyde was shown by Hinterberger¹³⁰ to cause the evolution of carbon monoxide. Conant, Webb and Mendum isolated isobutane from a sample of this compound allowed to decompose for many weeks in daylight in the absence of oxygen. By filter experiments, it was shown that light in the range 2950 to 3200 Å was effective. The addition of a small amount of hydroquinone decreased the decomposition to a third. Similar results were also obtained with dimethylacetaldehyde. Ultraviolet light also accelerated autoxidation of the trisubstituted aldehyde.

In the case of propionaldehyde, Leighton and Blacet¹³¹ reported results very similar to those for acetaldehyde. They indicated their belief that there may be two distinct primary processes, one of which occurring to the extent of 80 per cent or more yields directly $\text{R}\cdot\text{H}$ and CO , as postulated by Norrish. The other yields R_2 , hydrogen (which could be detected), and carbon monoxide. They also extended their work to include *n*- and *iso*-butyraldehyde.¹³²

The quantum yields in the case of acetaldehyde and propionaldehyde are

¹²⁴ Pearson, T. G., *J. Chem. Soc.*, 1718 (1934).

¹²⁵ Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 1151 (1935); 253 (1936); Glazebrook, H. H., and Pearson, T. G., *Ibid.*, 1777.

¹²⁶ Glazebrook, H. H., and Pearson, T. G., *J. Chem. Soc.*, 567 (1937).

¹²⁷ Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, 6, 911 (1929); *Brit. Chem. Abs.*, 1930A, 555.

¹²⁸ Discherl, W., *Z. physiol. Chem.*, 188, 225 (1930).

¹²⁹ Benson, G., and Cadenhead, A., *J. Soc. Chem. Ind.*, 54, 40 (1934).

¹³⁰ Hinterberger, H., Dissertation, Vienna, 1923; cited by Conant, J. B., Webb, C. N., and Mendum, W. C., *J. Am. Chem. Soc.*, 51, 1248 (1929).

¹³¹ Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, 54, 3165 (1932).

¹³² Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, 54, 3165 (1932); 55, 1766 (1933).

greatly reduced in the presence of small amounts of nitric oxide.¹³³ The photochemical decomposition of isovaleraldehyde involves two types of reactions, according to Norrish and Bamford.¹³⁴ One, in line with the usual Norrish mechanism, yields directly CO and isobutane and occurs to the extent of 47 per cent. The other, a new type of dissociation, gives rise to propylene and acetaldehyde, which then suffer further decomposition. In this case there is a rupture between the α and β carbon atoms of the hydrocarbon chain, producing an olefin and a simpler aldehyde. This type of reaction has been found to occur more readily in ketones than in aldehydes and is said to be facilitated by extending the length of the hydrocarbon chain.¹³⁵

Oxidation of Aldehydes. It has been claimed that per-acids may be obtained by treating aldehydes with oxygen, under the influence of chemically active rays.¹³⁶ Taylor and Gould¹³⁷ found the photooxidation of aqueous formaldehyde solutions to be a chain reaction. According to Carruthers and Norrish,¹³⁸ the process is



Part of the formic acid decomposes to water and carbon monoxide and part to hydrogen and carbon dioxide. 45 per cent of the formaldehyde yields formic acid, 20 per cent water and carbon monoxide, 3 per cent carbon dioxide and hydrogen, 32 per cent is polymerized and a slight amount is photolyzed. The latter process may be reduced by the presence of a trace of iodine vapor.

Acetaldehyde yields 59 per cent oxygen, 25 per cent carbon monoxide, 1.5 per cent ethylene, 4 per cent methane and a trace of hydrogen. The condensed products give the reactions of peroxides, and the compound $\text{CH}_3\text{CO.O.O.COCH}_3$ may be an intermediate product. The quantum efficiency of the process in the wave-length region 2480 to 2750 Å is 11 moles decomposed per quantum absorbed. (It is ten in the case of formaldehyde.) In the presence of nitrogen, the quantum efficiency for the formation of biacetyl is approximately 22. The formation of an intermediate peracetic acid had been postulated by Bowen and Tietz¹³⁹ who regarded it as the first step of a chain reaction. Its reaction with a molecule of acetaldehyde gives acetic acid, the formation of which had been noted by Bertholet and Gaudechon. On the other hand, its reaction with a second molecule of peracetic acid gives the comparatively stable intermediate peroxide the formula of which was given above. The rate of the reaction is, according to Bowen and Tietz, independent of the oxygen concentration and proportional to the acetaldehyde concentration and to the square root of the light intensity. It is essentially the same at various wave-lengths within the absorption band of the aldehyde. In hexane solutions, alcohol acts as an inhibitor and the reaction becomes directly proportional to the light intensity.

Further evidence for the chain nature of the oxidation of aldehydes both in light and darkness has been given by Bäckström,¹⁴⁰ who investigated par-

¹³³ Mitchell, J. W., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **159A**, 32 (1937).

¹³⁴ Norrish, R. G. W., and Bamford, C. H., *J. Chem. Soc.*, 1504 (1935).

¹³⁵ For the behavior of normal and isobutyraldehydes which, in the main, resemble acetaldehyde, see Leighton, P. A., Levanas, L. D., Blacet, F. E., and Rowe, R. D., *J. Am. Chem. Soc.*, **59**, 1843 (1937).

¹³⁶ Consortium für Elektrochemische Industrie, British Patent 16,849, July 22, 1913.

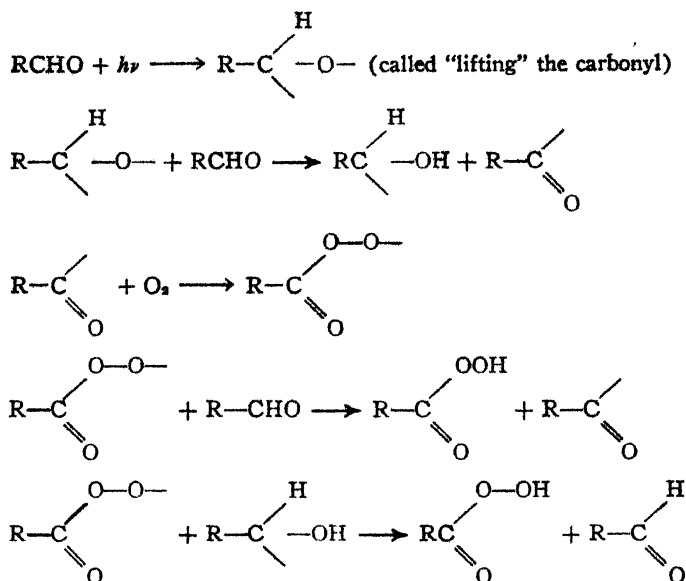
¹³⁷ Taylor, H. S., and Gould, A. J., *J. Phys. Chem.*, **37**, 367 (1933).

¹³⁸ Carruthers, J. E., and Norrish, R. G. W., *J. Chem. Soc.*, 1036 (1936).

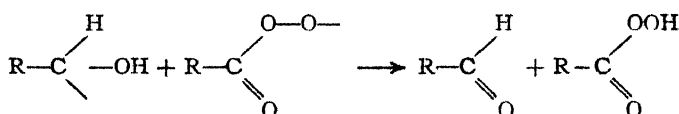
¹³⁹ Bowen, E. J., and Tietz, E. L., *J. Chem. Soc.*, 23 (1930); see also Cantieni, R., *Z. wiss. Phot.*, **36**, 119 (1937) for the formation of a peroxide during the irradiation of paracetaldehyde in oxygen.

¹⁴⁰ Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927).

ticularly benzaldehyde and enanthaldehyde. The maximum yields amounted to about 10,000 for the former and 15,000 for the latter. He has also shown that the ketone-sensitized oxidation¹⁴¹ of aldehydes has the same chain mechanism as the photochemical oxidation:



The chains are broken by the mechanism:



This mechanism was believed to be in agreement with the rates found by Bowen and Tietz in the case of gaseous acetaldehyde.

Bogert and McDonough¹⁴² have studied the rates of autoxidation of seventeen aldehydes used in perfumery. With the exception of salicylaldehyde, they are subject to autoxidation in daylight and in darkness, the daylight rates being, except in the case of the cinnamaldehyde types, considerably greater than those in darkness. The temperature coefficients were the same for both the light and dark reactions.

Unsaturated Aldehydes. Acrolein is unaffected by diffused daylight in two months when exposed in sealed tubes, but sunlight solidifies about one-third of it in quartz tubes in twelve days and the mercury arc completely solidifies it in 1½ hours.¹⁴³

Thompson and Linnett¹⁴⁴ have found its absorption spectrum to consist of two

¹⁴¹ Backström, H., *Z. physik. Chem.*, **B25**, 99 (1934).

¹⁴² Bogert, M. T., and McDonough, E. G., *Drug and Cosmetic Ind.*, **32**, 312, 332, 514, 533, 536, 538, 540 (1933); *Chem. Abs.*, **27**, 4625 (1933).

¹⁴³ Moureu, C., Murat, M., and Tampier, L., *Ann. chim.*, **15**, 221 (1921); *Compt. rend.*, **171**, 1267 (1921); *Chem. Abs.*, **15**, 2220 (1921); **16**, 55 (1922); Moureu, C., Dufraisse, C., and Badoche, M., *Bull. soc. chim.*, **35**, 1572, 1591 (1924) have also investigated its oxidation in light.

¹⁴⁴ Thompson, H. W., and Linnett, J. W., *Nature*, **134**, 937 (1934); *J. Chem. Soc.*, 1452 (1935).

widely separated regions. Between 3800 and 2900A there are bands with fine rotational structure, at least at the long-wave end, and no underlying continuum. No fluorescence, however, could be observed on irradiation within this region, but polymerization occurred. The maximum absorption was found at 3450A. The bands in the second absorption region beginning at 2350A were narrow and diffuse and probably accompanied by a continuum, at least at the shorter wave-lengths. Recently, Eastwood and Snow¹⁴⁵ have given detailed analyses of the spectrum of this and other aldehydes, including some saturated ones. Blacet, Fielding and Roof¹⁴⁶ state that in the region of sharp bands (3660-3130A) the quantum yield for polymerization is less than 0.5. At 3020A where the absorption is very diffuse, it is 1.0. On the border between banded and continuous absorption (2804A) it is 10, and in the continuous region at 2654-2537A, it is 19. Free radicals are assumed to play a part in the mechanism. There is an induction period. Irradiation also produces small quantities of acetylene but the quantum yield for dissociation is low, about 0.01 at 3665A.

Sigmund¹⁴⁷ held the theory that the presence of a carbon-to-carbon double bond, or a phenyl group, or of both together in an aldehyde molecule, stabilizes the carbonyl group, presumably in some manner by "partial valences." After saturation, the carbonyl group can be split off in the usual manner by the action of ultraviolet rays. Thus, hexahydrophenylacetaldehyde split off gas containing 80 per cent of carbon monoxide and hexahydrotoluene could be isolated. Hexahydro- β -phenylpropionaldehyde also eliminated carbon monoxide but at a lower rate. The residue consisted of higher polymerization products of the aldehyde, the trimer being isolated. Dodecylaldehyde gave a gas containing 80 per cent of carbon monoxide and in the residue $C_{11}H_{24}$ was identified.¹⁴⁸

A similar inertness has been found by Blacet and Roof¹⁴⁹ in crotonaldehyde which has an absorption spectrum resembling that of acetaldehyde shifted toward the red by several hundred A. It has discrete bands beginning at 3800A and continuing to 3245A where the bands begin to fade. From 3090 to approximately 2600A the absorption is apparently continuous. At 2550A a second region of continuous absorption begins and extends into the Schumann region. It is attributed to an electronic transition in the hydrocarbon end of the molecules. At 3660A only one quantum out of 150 was effective in causing a reaction, probably a polymerization. The wave-lengths 3130, 3020, 2804, 2654, 2537 and 2399A, all but the first of which are in regions of apparently continuous absorption, caused no detectable decomposition. Similar results were obtained when the aldehyde was subjected to the action of excited mercury atoms, but in the presence of oxygen a photochemical oxidation of the aldehyde vapors occurred.

Two explanations of this inertness in a region indicative of dissociation were suggested. The first, which relates the stability in some manner to the presence of conjugated double bonds, assumed that the absorption might be only apparently continuous, the energy of excitation being rapidly dissipated in other modes of vibration than that of the carbonyl group responsible for the absorption. More acceptable, however, would be the view that the continuous region implies, as usual, a true dissociation, but that this is followed by a rapid recombination. The need for the occurrence of three-body collisions may decrease in the case of such

¹⁴⁵ Eastwood, E., and Snow, C. P., *Proc. Roy. Soc.*, **149A**, 434, 446 (1935).

¹⁴⁶ Blacet, F. E., Fielding, G. H., and Roof, J. G., *J. Am. Chem. Soc.*, **59**, 2375 (1937).

¹⁴⁷ Sigmund, F., *Monatsh.*, **52**, 185 (1929).

¹⁴⁸ Müller, A., *Seifensieder-Ztg.*, **63**, 441 (1936); *Chem. Abs.*, **30**, 7556 (1936), notes a polymerization of phenylacetaldehyde in sunlight.

¹⁴⁹ Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58**, 73, 608 (1936).

a complex molecule, the excess energy going into some kind of excitation. This was believed to be in line with the fact that the quantum yields for decomposition of the higher saturated aldehydes are less than unity in the continuous absorption region, decreasing with increase in the molecular weight.

To summarize the reactions of the aldehydes,¹⁵⁰ it may be stated that some on activation dissociate to yield carbon monoxide and hydrocarbons, although a certain percentage of the molecules appear to dissociate to give free radicals.¹⁵¹ Furthermore, in the gas phase, the simpler aldehydes and ketones produce carbon monoxide and hydrocarbons, but the more complicated members tend to dissociate to yield simpler aldehydes or ketones and unsaturated hydrocarbons. Unsaturated aldehydes such as acrolein or crotonaldehyde are relatively inert.¹⁵² Recently, a number of aldehydes have been studied in aqueous solution by Farkas and Hirschberg.¹⁵³ The quantum yields for molecules destroyed are: formaldehyde, 0.5; acetaldehyde, 2.5; propionaldehyde, 1.8; crotonaldehyde, much less than one. In the case of acetaldehyde, acetaldol is formed; the formation of an aldehyde molecule with free valences may be the primary process.

Ketones. Berthelot and Gaudechon¹⁵⁴ found acetone to be rapidly decomposed by ultraviolet light, the gas formed having 49 per cent carbon monoxide, 46 per cent ethane and but 5 per cent methane. In aqueous solutions, carbon dioxide was also formed. With sunlight and air, acetic acid was also formed.¹⁵⁵

Henri and Wurmser¹⁵⁶ definitely showed the reaction to be related to the ultraviolet absorption spectrum of the carbonyl group.¹⁵⁷

At first it was believed¹⁵⁸ that absorption in the region about the maximum was continuous, Noyes¹⁵⁹ stating that no fine structure or discontinuities had been reported in the absorption curve even when long path-lengths of acetone vapor at low pressures were studied. He believed it an open question as to whether it is justifiable to assume that this implies a primary dissociation process in analogy with the continuous spectra of diatomic gases, since in such complex molecules resonance effects might lead to an overlapping of energy levels sufficient to preclude the appearance of any very marked banded structure. Noyes preferred to regard the primary process as of the type of predissociation by collision. More recently, however, Bowen and Thompson¹⁶⁰ using long

¹⁵⁰ Rollefson, G. K., *J. Phys. Chem.*, **41**, 259 (1937).

¹⁵¹ See, however, Norrish, R. G. W., and Bamford, C. H., *Nature*, **140**, 195 (1937). They also investigate the reactions in liquid paraffin solution at 100°, the products consisting of CO, RH and R'H, the latter being produced by dehydrogenation of the solvent by the alkyl radicals.

¹⁵² It has been observed by Kuhn, R., Badstubner, W., and Grundmann, C., [*Ber.*, **69B**, 98 (1936)] that pure crotonaldehyde does not undergo condensation with piperidine unless it has been exposed to sunlight or to a quartz lamp. The irradiation is believed to produce a compound, probably $\text{CH}_3\text{CH}=\text{CHCOOH}$, by autoxidation. This is thought to be necessary for the condensation.

¹⁵³ Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc.*, **59**, 2453 (1937).

¹⁵⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

¹⁵⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1164 (1910).

¹⁵⁶ Henri, V., and Wurmser, R., *Compt. rend.*, **155**, 503 (1912); see also Porter, C. W., and Iddings, C., *J. Am. Chem. Soc.*, **48**, 40 (1926) and Wiesler, K., *Z. anorg. Chem.*, **40**, 1023 (1927).

¹⁵⁷ Bowen, E. J., and Thompson, H. W., *Nature*, **133**, 571 (1934); Norrish, R. G. W., *Nature*, **133**, 837 (1934); Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (1934); Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, **B20**, 283 (1933). The influence of various substituents has been studied by Lowry, T. M., and Lishmund, R. E., [*J. Chem. Soc.*, 1313 (1935)] and by Herold, W., [*Z. physik. Chem.*, **B18**, 265 (1932); *Z. Elektrochem.*, **38**, 633 (1932)]. The effects of solvents of varying polarity have been described by Wolf, K. L., [*Z. physik. Chem.*, **2B**, 39 (1929)], Kremann, R., Pestemer, M., and Bernstein, P., [*Monatsh.*, **61**, 351 (1932)], and Pestemer, M., [*Z. Elektrochem.*, **40**, 493 (1934)].

¹⁵⁸ Ley, H., and Arends, B., *Z. physik. Chem.*, **12B**, 132 (1931); Scheibe, G., and Lindström, C. F., *Z. physik. Chem.*, **B12**, 387 (1931).

¹⁵⁹ Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 285 (1933). Noyes has recently attempted an interpretation of the near ultraviolet absorption spectrum, *Trans. Faraday Soc.*, **33**, 1495 (1937).

¹⁶⁰ Bowen, E. J., and Thompson, H. W., *Nature*, **133**, 571 (1934).

columns of acetone vapor at pressures of 0.5 to a few millimeters detected four groups of bands each composed of about 25 diffuse bands. Their centers were at 3150, 2900, 2710, and 2570Å. At higher pressures (up to about 200 mm.) the bands widened to produce a region of continuous absorption extending from 3200 to 2400Å, with its maximum at 2800Å, characteristic of compounds containing the carbonyl group. They discarded the hypothesis that predissociation splits a carbon-hydrogen or carbon-carbon bond, and attributed the diffuseness of the bands merely to an unresolved close packing of rotation lines, which they believed similar to that in the spectra of other Y-shaped molecules.

Further evidence came from a study of fluorescence. It was found by Damon and Daniels¹⁶¹ that acetone vapor shows a green fluorescence when irradiated by wave-lengths shorter than 3130Å. It is blue in the presence of a trace of oxygen, but changes to green when the latter has been removed by a photooxidation of some of the acetone. Norrish, Crone and Saltmarsh,¹⁶² found the absorption spectrum of acetone vapor to consist of a continuous band between about 3000 and 2200Å with a few faint maxima, and a region of discrete absorption between 3340Å and about 2950Å, thus slightly overlapping the continuous region. Fluorescence was produced only by absorption in the continuous region, its maximum intensity being excited by the absorption of the wave-length 3050Å. The fluorescence spectrum excited by the mercury arc consisted of three diffuse bands with maxima at 5100, 5600 and 6100Å.¹⁶³ The specific effect of oxygen was attributed to the removal of oxygen by excited acetone and the formation of a second transient fluorescent substance. The fluorescence of acetone vapor was unaffected by the addition of nitrogen, but its intensity increased with increasing pressure of acetone vapor.¹⁶⁴ The characteristics of the fluorescence were thought to argue against the concept that it arises from excited molecules of the usual type formed in the continuous region. Furthermore, the assumption of Bowen and Thompson that the apparently continuous bands are really composed of unresolved closely packed rotation lines would not account for the abrupt appearance of fluorescence observed to occur at the wave-lengths at which the diffuseness of the bands begins.^{164a}

Norrish suggested that the energy absorbed by the chromophoric carbonyl group passes to some other linking or linkings in the molecule by a process similar to the radiationless transfer in a collision of the second kind. A portion may lead to the formation of free radicals by decomposition, a portion may lead to a decomposition of the molecule by a process of the type discussed for aldehydes which produces carbon monoxide and ethane, and a portion, less than 3 per cent, may be lost by fluorescence.

Although Bowen and Watts,^{164b} who used nonmonochromatic light, reported a quantum yield of 1.8 for the photolysis of acetone vapor, Damon and Daniels¹⁶⁵ found it much lower, only about one of every five or six absorbed quanta leading to chemical reaction, including both decomposition and condensation processes. The yields were about the same for radiations of 3130 and 2650Å. Decreasing the

¹⁶¹ Damon, G. H., and Daniels, F., *J. Am. Chem. Soc.*, **55**, 2363 (1933).

¹⁶² Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (1934).

¹⁶³ The visible and diffuse fluorescence is accompanied also by ultraviolet emission of fine sharp lines, interpreted as predissociation in emission by Crone, H. G., and Norrish, R. G. W., *Nature*, **132**, 241 (1933). See also Padmanabhan, R., *Proc. Indian Acad. Sci.*, **5A**, 594 (1937); *Chem. Abs.*, **31**, 8379 (1937). Matheson, M. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **60**, 1857 (1938).

¹⁶⁴ But compare, Fisk, C. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **2**, 654 (1934).

^{164a} Norrish, R. G. W., *Nature*, **133**, 837 (1934).

^{164b} Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (1926).

¹⁶⁵ Damon, G. H., and Daniels, F., *J. Am. Chem. Soc.*, **55**, 2363 (1933).

intensity to about one-tenth increased the quantum yield by more than 50 per cent. Reducing the acetone pressure to one-tenth atmospheric reduced the quantum yield to roughly one quarter that at atmospheric pressure.

Condensation reactions occurred only in the presence of traces of moisture.¹ It was suggested that under these conditions diacetone alcohol was produced. The latter could be photolyzed by the wave-length 3650A to the same products of photolysis as those of acetone. The alcohol shows a green fluorescence when irradiated by the wave-lengths 3650, 4050 or 4360A, but only slight fluorescence at 3130A or shorter wave-lengths.

Damon and Daniels found the products of photolysis of acetone to include carbon monoxide, ethane, methane, hydrogen and free carbon. Their mechanism was based on the assumption that activated molecules split off carbon monoxide, the remaining methyl groups combining in more than half the molecules to form ethane. Norrish, Crone and Saltmarsh found 46.6 per cent carbon monoxide, 44.2 per cent ethane and 9.2 per cent of methane and confirmed the quantum yield measurements of Damon and Daniels. Light absorbed both in the regions of discrete and continuous absorption leads to decomposition, the yields being 0.2 at 3150A and 0.4 at 2650A. The full mercury arc gives somewhat less than 10 per cent of methane, possibly derived from a photoreaction in some liquid acetone also present. They believed the primary process to consist, as discussed in connection with their fluorescence observations, in the formation of free methyl radicals and the liberation of carbon monoxide. That the quantum yields were low, even in the continuous region, was accounted for only to a slight extent by the observed fluorescence. They preferred to conceive of the absorbed energy being for the most part degraded to heat by a process of internal stabilization in which the energy absorbed by the carbonyl group is divided up among the various forms of motion possible in the complex molecule. The theory of Norrish is of considerable importance in emphasizing the possibility that energy absorbed in producing an electronic transition in one part of a molecule need not remain localized if the molecule is complex. The energy absorbed by the carbonyl group amounts to about 90 kcal. It is then partly transferred by resonance to the part of the molecule to be decomposed, about 25-65 kcal. being required for each linkage to be broken. The formation of carbon monoxide suggested the simultaneous breaking of two linkages.¹⁶⁶

Spence and Wild¹⁶⁷ believe that at temperatures below 60°, the primary process may consist in the rupture of but one linking with the formation of methyl and the acetyl radicals, since they were able to isolate large volumes of biacetyl from the liquid products of the photolysis of acetone. They found the ratio of the volume of ethane produced to that of carbon monoxide to be 1.5. At higher temperatures, however, the ratio is unity, and some methane is formed,¹⁶⁸ suggesting that under these conditions, the acetyl radical is short-lived. In the banded absorption region, the decomposition is slow and the ethane to carbon monoxide ratio is nearly one.

The reaction is increased by an increase of temperature, Winkler¹⁶⁹ finding

¹⁶⁶ Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, 3, 171 (1935); *Chem. Abs.*, 30, 2493 (1936).

¹⁶⁷ Spence, R., and Wild, W., *Nature*, 138, 206 (1936); *J. Chem. Soc.*, 352 (1937).

¹⁶⁸ See also Taylor, H. S., and Rosenblum, C., [*J. Chem. Phys.*, 6, 119 (1938)], who investigated the reaction in the presence of hydrogen. They believe the major primary process to be dissociation to methyl radicals, and consider especially the activation energies of the secondary processes, concluding the ethane to result either from a wall reaction with zero activation energy or from a bimolecular process of small activation energy.

¹⁶⁹ Winkler, C. A., *Trans. Faraday Soc.*, 31, 761 (1935).

the quantum yield at 100°C. to be five times that at 60°C. This higher yield is maintained up to 400°C. The effect of temperature is much greater when the irradiation is by longer wave-lengths than by shorter ones. This may be due to the fact that the thermal energy of the molecule contributes more to the dissociation process when small quanta are absorbed than when larger ones are employed. At 400°C., the reaction products included a considerable quantity of methane and unsaturated compounds, indicative of the photochemical formation of ketene, $\text{CH}_2=\text{C}=\text{O}$. Leermakers¹⁷⁰ also found the quantum yield for carbon monoxide formation to be nearly unity in the temperature range 200° to 400°C., the carbon monoxide in the reaction products decreasing from 50 per cent to approximately 33 per cent. He also found that methyl radicals do not initiate a chain decomposition of acetone below 400°C.

Mention has not yet been made of the fact that the absorption by acetone increases from a minimum at about 2115Å toward shorter wave-lengths, photolysis being pronounced below 2000Å.¹⁷¹ A vibrational analysis of the group of bands extending from 1960 to about 1800Å has been given by Noyes, Dunning and Manning,¹⁷² who photographed the spectrum down to 1200Å and found other bands ascribed to different electron transitions below 1800Å. According to Manning,¹⁷³ wave-lengths in the range 1900-2000Å have little effect on acetone at pressures around 100 mm. The most effective ones are those shorter than 1700Å; these produce increased amounts of hydrogen. At very low pressures (0.025 mm.), however, wave-lengths in the range 1850 to 2000Å are more effective, but form only small amounts of gaseous hydrocarbons. The presence of a condensed non-volatile hydrocarbon was suspected. Howe and Noyes¹⁷⁴ find that in this range the quantum yield is independent of the intensity, but increases with decreasing acetone pressure to a limit of 0.65. It is increased by the addition of nitrogen, ethane or carbon dioxide.

In hexane solution, the rate of decomposition is less than when the acetone is in the vapor form, and the quantum yield decreases with increasing acetone concentration.¹⁷⁵ Gases are not evolved and the chief products are a substance capable of absorbing bromine readily, and an alcohol, probably dimethyl-*n*-hexyldimethylcarbinol. Similarly, the reaction in carbon tetrachloride as solvent evolves no gas. In benzene solution, no photochemical reaction occurs.

In an aqueous solution, the production of formaldehyde as well as of acetic acid has been noted by Qureshi and Taher.¹⁷⁶ The quantum yields varied between 0.13 and 0.14 for concentrations 0.05 to 0.5 molar in acetone. The temperature coefficient of the rate was 1.52.¹⁷⁷

Berthelot and Gaudechon¹⁷⁸ observed that one cc. of a 10-per cent solution of dihydroxyacetone evolved 0.2 cc. of almost pure carbon monoxide during 12 hours of exposure to sunlight. They also studied the behavior of diethylketone.¹⁷⁹

¹⁷⁰ Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1899 (1934).

¹⁷¹ Ley, H., and Arends, B., *Z. physik. Chem.*, **12B**, 132 (1931).

¹⁷² Noyes, W. A., Jr., Dunning, A. B. F., and Manning, W. M., *J. Chem. Physics*, **2**, 717 (1934); **3**, 131 (1935); Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

¹⁷³ Manning, W. M., *J. Am. Chem. Soc.*, **56**, 2589 (1934).

¹⁷⁴ Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

¹⁷⁵ Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934); Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1685 (1936).

¹⁷⁶ Qureshi, M., and Taher, N. A., *Nature*, **127**, 522 (1931); *J. Phys. Chem.*, **36**, 2670 (1932).

¹⁷⁷ For the photooxidation of acetone vapor, see P. Fugassi, *J. Am. Chem. Soc.*, **59**, 2092 (1937).

¹⁷⁸ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 401 (1912).

¹⁷⁹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

Norrish and Appleyard¹⁸⁰ found that, in the light of a mercury arc, about 80 per cent of the molecules of methylethylketone which decompose yield carbon monoxide and a mixture of ethane, propane and butane, the remainder forming ethylene and acetaldehyde.¹⁸¹ Methylbutylketone yielded propene and acetone. In the range 2480 to 2770 Å the quantum yield of the decomposition of this ketone at 760 mm. and 127°C. by the process yielding carbon monoxide, methyl and butyl radicals is approximately 0.03, and by that yielding acetone and methylethylene, 0.27. That for condensation or polymerization is approximately 0.04.¹⁸²

The absorption spectrum is diffuse and fluorescence is not observed. Similarly, dipropylketone exhibits two types of change on irradiation.¹⁸³ One type (37 per cent of the molecules decomposed) yields carbon monoxide and hexane, and the other (63 per cent) forms ethylene and methylpropylketone. In this reaction, Pearson and Purcell¹⁸⁴ detected the formation of the propyl radical by the mirror test and gave its half-life period as 2.3×10^{-8} second. In cyclohexanone, 10-per cent solutions of methylbutyl ketone and dipropylketone yield 98 per cent of methylethylene and ethylene, respectively, at 20°C. But at 100°C., dipropylketone gave also carbon monoxide and ethane. Two mechanisms accordingly seem necessary. One involves activated molecules with relatively long lives which are readily destroyed by collisions with the solvent molecules. The other involves excited molecules of such short life that the solvent molecules have no time to intervene between the time of activation and the subsequent decomposition.¹⁸⁵

Saltmarsh and Norrish¹⁸⁶ have decomposed the vapors of cyclopentanone, cyclohexanone and cycloheptanone in the light of a quartz mercury arc. From 80 to 95 per cent of the last-named ketone decomposed to give cyclohexane and carbon monoxide and 4 per cent went to methylethylene. Of the cyclohexanone, 92 per cent gave carbon monoxide and cyclopentane and 8 per cent went to ethylene, methylethylene and carbon monoxide. Half of the cyclopentanone gave ethylene and carbon monoxide and half went to a mixture of propylethylene, *sym*-dimethylethylene and carbon monoxide.

Irradiation of isopropenylmethyl ketone by means of a quartz lamp produces in five days a solid polymer, soluble in acetone and precipitated as a colorless powder by methyl alcohol.¹⁸⁷ Under the same conditions, neither propenylmethylketone nor mesityl oxide polymerizes. The polymerization could take place by 1,4-addition as with rubber, through the carbonyl group analogous to the polyoxymethylenes and by the ethylene linkage with the formation of a paraffin derivative. Combinations of these methods of polymerization would lead to three-dimensional structures, but the solubility of the product did not support the occurrence of such a complication. The molecular weight of the polymer, as determined by the Staudinger viscosity method, was 34000.

¹⁸⁰ Norrish, R. G. W., and Appleyard, M., *J. Chem. Soc.*, 874 (1934). For results at 100° in liquid paraffin solution, see Norrish, R. G. W., and Bamford, C. H., *Nature*, 140, 195 (1937); Norrish, R. G. W., *Trans. Faraday Soc.*, 33, 1521 (1937). Here the free radicals react mainly with the solvent rather than combine together.

¹⁸¹ At 3130 Å, 11 per cent of the reaction goes to diketones. Biacetyl is also formed when the irradiation is in the range 1850 to 2000 Å. In this range the quantum yield for carbon monoxide formation increases from 0.7 to 0.88 as the pressure decreases from 90 mm. to 0.1 mm. The total quantum yield for the decomposition approaches unity at low pressures. Ellis, V. K., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, 60, 2031 (1938).

¹⁸² Bloch, B. M., and Norrish, R. G. W., *J. Chem. Soc.*, 1638 (1935).

¹⁸³ Bamford, C. H., and Norrish, R. G. W., *J. Chem. Soc.*, 1504 (1935).

¹⁸⁴ Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 253 (1936).

¹⁸⁵ Norrish, R. G. W., and Bamford, C. H., *Nature*, 138, 1016 (1936).

¹⁸⁶ Saltmarsh, O. D., and Norrish, R. G. W., *J. Chem. Soc.*, 455 (1935); see also Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, 3, 171 (1935); *Chem. Abs.*, 30, 2493 (1936).

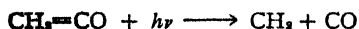
¹⁸⁷ Staudinger, H., and Ritzenthaler, B., *Ber.*, 67B, 1773 (1934).

According to Bowen and de la Praudière,¹⁸⁸ liquid benzophenone at 100°C., showed no change after irradiation for nine hours with a mercury arc, and acetophenone no change after seven hours. When a 0.1 molar solution of benzophenone in hexane was irradiated, benzopinacol crystallized out, being formed with a quantum efficiency of 0.04. None was formed when carbon tetrachloride was the solvent.

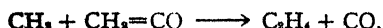
The quantum efficiency of the photopolymerization of biacetyl in solutions in hexane or ether by wave-lengths between 4360 and 3660A is greater the more dilute the solutions. Bowen and Horton¹⁸⁹ account for this by an explanation which Bowen also used to account for the more rapid decomposition of various ketones in solution than in the pure liquid state. This was to the effect that the primary excited level is not reactive but passes, if not deactivated by a collision within 10⁻¹² second, into a second excited level which is reactive.

Ketene. The absorption spectrum of ketene vapor consists of a series of regularly spaced diffuse bands in the region of carbonyl absorption, 3700 to 2600A. The maximum absorption is somewhat displaced to longer wave-lengths occurring at 3100A.¹⁹⁰ No difference exists between the absorption spectra of aldoketenes of the type H₂C=CO and ketoketenes, R₂C=CO. There is also a region of continuous absorption beginning at 2200A and ascribed to the ethylene linking. Fluorescence is lacking in ketene.

Irradiation with the mercury arc leads to decomposition with the formation of two volumes of carbon monoxide and one of ethylene. Norrish, Crone and Saltmarsh believe that light energy absorbed by the carbonyl group is transferred to the ethylene group with consequent rupture.



This is followed by the process:



Ross and Kistiakowsky¹⁹¹ interpreted the above-mentioned primary process as due to predissociation in accordance with the nature of the absorption spectrum, no collisions being necessary. They found the decomposition to occur with a quantum yield of approximately unity at 3130A. The accumulation of ethylene stops the reaction. A solid film deposited on the walls of the reaction vessel must have the composition (CH₂)_n since no free carbon deposits were obtained and no hydrogen was liberated.

Ross and Kistiakowsky thought the additional energy required to break the double bond over that available in the absorbed quantum might be derived from the resonance energy of the carbon monoxide formed in the decomposition. The secondary reaction of Norrish was rejected because the quantum yield proved to be unity. The methylene radicals formed in the primary process must react with each other to form ethylene. The slowing down of the reaction by ethylene must be ascribed to the reaction of methylene groups with ethylene with formation of the solid polymer. Thus, methylene radicals appear to combine readily to ethylene in a bimolecular reaction, although methyl radicals do not combine so readily to form ethane. At 3660A, where the banded structure is more pronounced and

¹⁸⁸ Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934).

¹⁸⁹ Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1505 (1934).

¹⁹⁰ Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1533 (1933); Lardy, G. C., *J. chim. phys.*, 21, 353 (1924).

¹⁹¹ Ross, W. F., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, 56, 1112 (1934).

predissociation less probable, the quantum yield of the reaction, which occurs but slowly at this wave-length, appears to be less than unity.

Norrish, Crone and Saltmarsh¹⁹² do not agree that the observed quantum yields necessarily exclude the occurrence of their secondary reaction, since it is known that in polyatomic molecules, as acetone, etc., the quantum yield of the primary process may be less than unity throughout a considerable portion of a region of continuous absorption.

Diketones. In α -dicarbonyl compounds, such as glyoxal, the conjugation of the double bonds moves the absorption into the visible.¹⁹³ Glyoxal vapor, which has its maximum absorption between 4550 and 4123A, gives as the main products of decomposition carbon monoxide and a solid consisting of a polymer of the hitherto unknown glycerosone, $\text{CH}_2\text{OH}\cdot\text{CO}\cdot\text{CHO}$. About 2 per cent of hydrogen was also obtained as a result of a second reaction.¹⁹⁴

Schwenk and Borgwardt¹⁹⁵ prepare unsaturated α , β -diketones by subjecting aromatic, hydroaromatic or aliphatic compounds in which a methylene group is directly coupled to an ethylene linkage, to the action of selenium dioxide and ultraviolet rays without heating. Thus, from α -indene is produced a ketone, $\text{C}_{10}\text{H}_{14}\text{O}$.

Biacetyl vapor is decomposed by ultraviolet rays with the production of ethane and carbon monoxide. An aqueous solution yields acetic acid and acetaldehyde.¹⁹⁶ Observations by Grossmann¹⁹⁷ on the absorption spectrum of ethylacetoacetate show that it is decomposed by ultraviolet rays, yielding mainly ethyl acetate and acetic acid. Under the same conditions, acetylacetone gives acetic acid and acetone.¹⁹⁸ Vitoria¹⁹⁹ finds that light from a quartz lamp causes partial polymerization and decomposition of gaseous acetylacetone with formation of carbon monoxide. With light of wave-lengths longer than 3050A, only polymerization occurs. Liquid acetylacetone, or its solution in carbon tetrachloride, undergoes a decided polymerization, but does not decompose to yield carbon monoxide. Walker and Wild²⁰⁰ find acetyl peroxide to yield on photochemical decomposition, carbon dioxide, methane and some ethane.

Carbohydrates. In contrast to the observations of Bielecki and Henri²⁰¹ and of Niederhoff,²⁰² Henri and Schou²⁰³ found that solutions of very pure dextrose showed no indication of an absorption band due to the carbonyl group at 2800A, most of the molecules having a ring structure. Alkaline solutions, however, exhibit the band, the number of molecules in the aldehydic form depending on the age, temperature and pH of the solution. Similar conclusions have

¹⁹² Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Am. Chem. Soc.*, **56**, 1644 (1934).

¹⁹³ Lüthy, A., *Z. physik. Chem.*, **107**, 302 (1923); Purvis, J. E., and McClelland, N. P., *J. Chem. Soc.*, **101**, 1810 (1912); Neuberger, C., and Schou, S. A., *Biochem. Z.*, **191**, 466 (1927); Marchlewski, L., Pizlo, J., and Urbanczyk, W., *Biochem. Z.*, **264**, 437 (1933).

¹⁹⁴ Norrish, R. G. W., and Griffiths, J. G. A., *J. Chem. Soc.*, 2829 (1928).

¹⁹⁵ Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935, to Schering-Kahlbaum, A.-G.; *Chem. Abs.*, **29**, 6246 (1935).

¹⁹⁶ Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, **45**, 1827 (1923).

¹⁹⁷ Grossmann, P., *Z. physik. Chem.*, **109**, 305 (1924); *Chem. Abs.*, **19**, 39 (1925).

¹⁹⁸ Morton, R. A., and Rosney, W. C., *J. Chem. Soc.*, 706, 713 (1926) and Acly, H. E., and French, H. S., *J. Am. Chem. Soc.*, **49**, 847 (1927) report absorption data on these and related compounds. The enolic and ketonic forms are distinguishable by bands near 2500 and 2700A, respectively.

¹⁹⁹ Vitoria, A. P., *IX Congr. intern. quim. pura applicata*, **2**, 334 (1934); *Chem. Abs.*, **29**, 7811 (1935).

²⁰⁰ Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (1937).

²⁰¹ Bielecki, J., and Henri, V., *Ber.*, **46**, 3627 (1914).

²⁰² Niederhoff, P., *Z. physiol. Chem.*, **165**, 130 (1927); **167**, 310 (1927); **174**, 300 (1928).

²⁰³ Henri, V., and Schou, S. A., *Z. physiol. Chem.*, **174**, 295 (1928).

been reported for a number of other sugars, including galactose, levulose, *l*-arabinose, rhamnose, maltose and lactose.²⁰⁴

The variations in the absorption exhibited by these sugars under various conditions of pH and the effects of impurities may perhaps account for the diverse statements which have been made in regard to their susceptibilities to photolysis. It is generally agreed that aqueous solutions of dextrose, galactose and mannose are not affected by sunlight, although changes²⁰⁵ may be produced in the presence of such sensitizers as iron or uranium salts.²⁰⁶ Ghosh and Rakshit²⁰⁷ claim that visible light increases somewhat the rate of oxygen absorption by glucose or fructose in the presence of cerium hydroxide as catalyst.

Irradiation of 0.1 to 50 per cent glucose solutions with a mercury-vapor arc for fifteen minutes to five hours causes, according to Dillman,²⁰⁸ no apparent change in optical rotation nor in their ability to reduce alkaline copper tartrate solution. de Fazi²⁰⁹ believed that sugar solutions which had been irradiated six hours fermented more rapidly than untreated solutions. The induced oxidation of glucose by glutathione is said to be markedly accelerated by light; photosensitizers further accentuate the reaction.²¹⁰

The formation of acid in irradiated dextrose solutions was noted by Euler and Lindberg,²¹¹ who showed that on further action of the ultraviolet rays, there resulted a gaseous mixture containing 15 per cent carbon dioxide, 40 per cent carbon monoxide and 40 per cent hydrogen. Berthelot and Gaudechon,²¹² however, found approximately equal volumes of carbon monoxide and methane and about six times as much hydrogen. More recently, Bernoulli and Cantieni²¹³ noted that at the beginning of the reaction much more hydrogen than carbon monoxide is evolved, but that later the reverse is true. The decomposition was accelerated by acids and retarded by alkalies. No optically active decomposition products were formed, and the decrease in glucose as measured by rotation was not proportional to the amount of carbon monoxide evolved.

Ketoses were found by Berthelot and Gaudechon,²¹⁴ to undergo photolysis more readily, and to behave in a manner similar to that of acetone. Levulose, sorbose, perseulose, crythrulose and dihydroxyacetone each gave carbon monoxide, hydrogen and the alcohol with one carbon atom less than the parent sugar. Extreme ultraviolet rays caused secondary reactions, in which carbon dioxide and methane were

²⁰⁴ Marchlewski, L., and Kwienicinski, L., *Bull. Acad. Polonaise*, 255, 1926A; 379, 1927A; 257, 263, 271, 1928A; 317, 1929A; *Bull. soc. chim.*, 43, 725 (1928); *J. physiol. Chem.*, 169, 300 (1927); Marchlewski, L., and Gabryelski, W., *Bull. Acad. Polonaise*, 397, 1933A; Marchlewski, L., and Urbanczyk, W., *Ibid.*, 409, 1933A; *Biochem. Z.*, 261, 393 (1933); Fischler, F., Hauss, H., and Taufel, K., *Biochem. Z.*, 265, 181 (1933); Braun, E., *Ber.*, 63B, 1972 (1930); Kwienicinski, L., Mayer, J., and Marchlewski, L., *Z. physik. Chem.*, 176, 292 (1928); Bednarczyk, W., and Marchlewski, L., *Bull. Acad. Polonaise*, 140, 1937A; *Chem. Abs.*, 32, 1576 (1938); Goos, F., Schlubach, H., and Schroter, G., *Z. physik. Chem.*, 186, 148 (1930). For absorption data on glucosides, see Marchlewski, L., and Mayer, J., *Bull. Acad. Polonaise*, 111 (1929); Ramart-Lucas, Mme., and Rabate, J., *Compt. rend.*, 196, 1493 (1933). For hexose phosphates, Neuberg, C., and Schou, S. A., *Biochem. Z.*, 191, 466 (1927).

²⁰⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, 155, 831 (1912)

²⁰⁶ Neuberg, C., *Biochem. Z.*, 39, 158 (1912); Abelous, Aloy and Valdiguè, *Compt. rend. soc. biol.*, 96, 1385 (1927).

²⁰⁷ Ghosh, J. C., and Rakshit, P. C., *J. Indian Chem. Soc.*, 12, 357 (1935); *Brit. Chem. Abs.*, 1935A, 1329.

²⁰⁸ Dillman, L. M., *J. Lab. Clin. Med.*, 17, 236 (1931); *Chem. Abs.*, 26, 3270 (1932).

²⁰⁹ de Fazi, R., *Atti accad. Lincei*, 5, 344, 901 (1927); *Chem. Abs.*, 21, 4013 (1927); Sanzo, L., and Pirrone, F., *Atti accad. Lincei*, 13, 613 (1931); *Chem. Abs.*, 26, 2990 (1932).

²¹⁰ Palit, C. C., and Dhar, N. R., *J. Indian Chem. Soc.*, 11, 661 (1934); *Brit. Chem. Abs.*, 1934A, 1314. See also *J. Phys. Chem.*, 32, 1263 (1928).

²¹¹ Euler, H., and Lindberg, E., *Biochem. Z.*, 39, 410 (1912); *J. Chem. Soc.*, 102, II, 407 (1912).

²¹² Berthelot, D., and Gaudechon, H., *Compt. rend.*, 151, 395 (1910).

²¹³ Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta*, 15, 119 (1932).

²¹⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, 155, 401, 1153 (1912); *Bull. soc. chim.*, 35, 241 (1924); see also Beyersdorfer and Hess, *Ber.*, 57B, 1708 (1924).

evolved and the solution became acid. Levulose gave about ten times as much carbon monoxide as of methane.²¹⁵ Maltose behaved similarly to dextrose and sucrose gave results intermediate between dextrose and levulose.

The decomposition of the latter sugar gave also formaldehyde and methanol.²¹⁶ It was believed that this sugar was very slowly decomposed by sunlight, 0.54 cc. of almost pure carbon monoxide being produced in two months.²¹⁷

The use of this behavior of a 10 per cent fructose solution in ultraviolet actinometry, proposed by Berthelot and Gaudechon,²¹⁸ has been more recently studied by Bernoulli and Cantieni.²¹⁹ In dilute solutions (4.5 to 18 g. per liter), the velocity is proportional to the concentration but in strong ones (720 to 1080 g. per liter), it is constant. The proportion of carbon dioxide in the gases evolved varies inversely with the light intensity. Acids appear to be formed only in solutions heated to 80°C. The evolution of gases is accelerated by sodium chloride and retarded by potassium bromide and iodide and acids or bases. The photolysis also occurs in methanol or glycerol solutions and in these is more accelerated by small amounts of water than by larger ones. The reaction can be produced by radiations passing through glass, but is much slower than in quartz, since only those fructose molecules possessing the ketonic structure evolve carbon monoxide. Molecules with ring structures are believed to yield carbon dioxide. At ordinary temperatures, the reaction, once started, may continue for hours after stopping the irradiation, but at high temperatures, the after-effect is very slight. The course is believed to involve the intermediary formation of a peroxide, perfructose. A yellow color (photopyridine) developed by light in solutions of pyridine, water and fructose is more readily formed and more readily bleached than it is in solutions in which the fructose is replaced by glucose, galactose, sucrose or lactose. Acetone inhibits its formation. Methanol is almost without influence on the color reaction, but has a greater retarding influence on fading than has fructose. Pure ethanol retards color formation, but the color once formed is more stable in ethanol than in methanol.

Holtz²²⁰ finds the ultraviolet irradiation of aqueous sugar solutions (glucose, fructose, arabinose) and sugar-like solutions (glycerol, sorbitol, glucosamine) to produce substances which form systems with strong negative redox potentials. The products are believed to accelerate the autoxidation of cysteine and adrenaline. Dubouloz²²¹ added eosin (1:5000) to a 0.05 molar solution of glucose in a phosphate buffer solution of pH 7.7, and freed the solution of dissolved oxygen. After sufficient illumination by a tungsten lamp, the oxidation-reduction potential descended to -210 mv., the equilibrium point of oxygen-free glucose solutions. Further illumination caused a further descent. If this did not exceed 350 mv., the phenomenon was reversible, and upon standing in the dark, the value -210 mv. was regained.

The oxidation of glucose by hydrogen peroxide in acid medium photosensitized by tungstic acid appears to follow the unimolecular rate law when the peroxide concentration is low and to be of zero order when it is high.²²² There is an

²¹⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 395 (1910).

²¹⁶ Bierry, H., Henri, V., and Ranc, A., *Compt. rend.*, **151**, 316 (1910); *Biochem. Z.*, **64**, 257 (1914); *Bull. soc. chim.*, **35**, 771 (1924).

²¹⁷ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 401 (1912).

²¹⁸ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 707 (1913).

²¹⁹ Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta*, **15**, 119 (1932); Cantieni, R., *Ibid.*, **17**, 1528 (1934); **18**, 473, 933, 1420 (1935); **19**, 86, 94, 270, 276 (1936); *Ber.*, **69B**, 2286 (1936).

²²⁰ Holtz, P., *Arch. expil. Path. Pharmacol.*, **182**, 141 (1936); *Brit. Chem. Abs.*, **1936A**, 1094.

²²¹ Dubouloz, P., *Compt. rend. soc. biol.*, **116**, 435 (1934); *Chem. Abs.*, **28**, 6371 (1934).

²²² Banerjee, T., *J. Indian Chem. Soc.*, **14**, 59 (1937); *Chem. Abs.*, **31**, 5275 (1937). See also Ghosh, J. C., and Mukherjee, J., *Ibid.*, **6**, 231 (1929).

induction period, which increases with the peroxide concentration. The velocity varies as the square root of the intensity of absorbed light, but is independent of the glucose concentration. The quantum yield is somewhat greater than unity and the temperature coefficient, 1.1 to 1.2. Similar reactions occur with formaldehyde and fructose.

Neutral solutions of sucrose are hydrolyzed by ultraviolet light and become slightly acid.²²⁸ The rate of hydrolysis increased with the duration of the exposure, probably because of the acid formation, although this may have been due to traces of a catalyst. According to Bierry, Henri and Ranc,²²⁴ the ultraviolet hydrolysis is appreciable in 5 per cent sucrose solutions after twenty hours of irradiation at 40°C.; after 48 hours formaldehyde can be detected. A gas evolution begins after 72 hours and becomes marked on the fifth or sixth day of exposure. Of the combustible part of this gas, 50 per cent was carbon monoxide.

Berthelot and Gaudechon,²²⁸ confirmed the presence of two stages in the hydrolysis of disaccharides by relatively long wave-lengths. The first stage does not evolve gas, but the second consists in the decomposition of the mixture of monoses produced in the first stage and so is accompanied by the evolution of gas. They disagreed with previous observers, in that they did not find that acid is formed during the process. Beyersdorfer and Hess²²⁶ using carefully purified sucrose and conductivity water found that at 15-20°C. in $\frac{1}{2}$ molar solution, the effect of irradiation was hardly perceptible. At 70° and 100°C., the sugar was attacked energetically, the decomposition at first increasing slowly, then rapidly, with increasing temperature. After the addition of 0.3 to 0.6 gram of chlorophyll to 250 cc. of $\frac{1}{2}$ molar solution, irradiation for twelve hours at 100°C. produced no detectable change in the sucrose. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide had little influence on the change, which, however, scarcely occurs in the presence of sodium acetate.

In 0.5 molar solution at 100°C., gas evolution begins in 15 minutes, and the acidity and reducing power increase about in proportion to the time. After about four hours, the solution becomes levorotatory and after 24 hours contains no further positively detectable amounts of optically active substances. The reducing power reaches its maximum after about 48 hours, then decreases proportionately with the time and more slowly than it had increased. A crystal of sucrose when exposed to ultraviolet rays at 70°C. becomes coated on the exposed surface with a brown layer of caramel.

Yajnik, Goyle and Wadhera²²⁷ maintain that aqueous sucrose solutions contained in Jena glass vessels undergo inversion when exposed to tropical sunlight in the absence of acid, and that in the presence of 0.25 normal acid, the rate of inversion is increased by sunlight. Some have believed visible and near infrared rays to effect the inversion with a high quantum yield, the reaction having also a high temperature coefficient.²²⁸ Tanret²²⁹ finds sucrose to be hydrolyzed slowly and maltose and trehalose to be hydrolyzed less than 30 per cent as fast as sucrose

²²⁸ v. Euler, H., and Ohlsen, H., *J. chim. phys.*, **9**, 416 (1911).

²²⁴ Bierry, H., Henri, V., and Ranc, A., *Compt. rend.*, **152**, 1629 (1911).

²²⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1016 (1912); **156**, 468 (1913).

²²⁶ Beyersdorfer, P., and Hess, W., *Ber.*, **57B**, 1708 (1924); Taketomi, N., and Miura, K., *J. Soc. Chem. Ind. Japan*, **33**, 9B (1930).

²²⁷ Yajnik, N. A., Goyle, D. N., and Wadhera, M. L., *Z. anorg. Chem.*, **225**, 24 (1935).

²²⁸ Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **6**, 879 (1929); *Brit. Chem. Abs.*, **A**, 555 (1930); *Z. anorg. Allgem. Chem.*, **199**, 1 (1931); see also Andant, A., and Rousseau, E., *Compt. rend.*, **186**, 365 (1928).

²²⁹ Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936).

²³⁰ Szalay, S., *Magyar Biol. Kutato Intezet Munkai*, **8**, 417 (1935-6); *Chem. Abs.*, **30**, 7041 (1936).

by ultraviolet rays. The effect on lactose was uncertain. Szalay²⁸⁰ suggested that pure sucrose solutions were not affected, but that those containing traces of glucose as catalyst, showed increased reducing power and acidity, ascribed by him to the formation of glucuronic acid.

Souty²⁸¹ directed two pencils of light from the same source, differing only in the direction of their circular polarization, on two identical solutions of a sugar which exhibits mutarotation. Differences in the rate of mutarotation, giving temporary differences which reached more than 0.25° were observed, but the same final equilibrium was obtained. In monochromatic light, glucose gave a positive result at 5461Å and a negative one at 5890-6Å.

In the case of the trioses, raffinose, melesitose and gentianose, the first stage of the reaction did not appear to consist of the formation of a monose and a biose.²⁸² After the first stage of decomposition, the action was the same as in the case of the monoses.

When a concentrated aqueous solution of trihexosan is exposed to ultraviolet rays for 56 hours, 60 per cent conversion into hexahexosan occurs; further irradiation of the latter appears to have no action.²⁸³ Irradiation of dextrinose, $C_{12}H_{20}O_{10}$, affords hexahexosan.

Massol²⁸⁴ stated that if solutions of soluble starch (prepared by heating for three hours at $150^\circ\text{C}.$) of 0.2 to 1 per cent concentration, are exposed at a distance of 10 centimeters, to the action of a mercury-vapor quartz lamp consuming 300 watts, the starch gradually loses the property of giving a blue color with iodine, the color undergoing an alteration similar to that observed when the iodine test is applied at various stages of starch conversion. The rate of transformation increases on decreasing the concentration and on acidifying the medium. As a result of the exposure also, the solution acquires reducing power (probably due to maltose) and becomes less precipitable by alcohol. The portion soluble in alcohol possesses reducing power and is dextrorotatory. The hydrolysis was not due to the acidity or temperature or to the small amount of hydrogen peroxide formed under the action of the rays. According to Bielecki and Wurmser,²⁸⁵ the hydrolysis is accompanied by a partial oxidation, since there can be identified among the products, besides dextrans, reducing sugars, including pentoses, some formaldehyde and other similar substances.

Samec²⁸⁶ found that on exposing thin layers of potato starch in presence of air to the rays of a quartz lamp, it became yellow and the odor of acraldehyde was observed. The properties of solutions obtained by heating starch so treated under pressure with water indicate that considerable peptization had occurred, together with a certain amount of oxidation and hydrolysis. The behavior on electrodialysis depends on the length of exposure to the ultraviolet, the amount of "gel" being smaller the longer the exposure. The phosphorus of the starch remains largely in organic combination. The cleavage products separated by ultrafiltration, although possessing a lower optical rotation, show the typical iodine colorations of the amylo-compound. Observations have also been made at $50^\circ\text{C}.$ on starch which has been previously dried, or washed with hydrochloric acid and dried and exposed to ultraviolet light in a stream of dry nitrogen and in

²⁸¹ Souty, P., *Compt. rend.*, **199**, 198 (1934).

²⁸² Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1506 (1912).

²⁸³ Pictet, A., and Vogel, H., *Rec. trav. chim.*, **48**, 843 (1929); *Brit. Chem. Abs.*, **1929A**, 1167.

²⁸⁴ Massol, L., *Compt. rend.*, **152**, 902 (1911).

²⁸⁵ Bielecki, J., and Wurmser, R., *Compt. rend.*, **154**, 1429 (1912).

²⁸⁶ Samec, M., *Kolloid. Chem. Beih.*, **23**, 377 (1927); *Brit. Chem. Abs.*, **A**, 412 (1927).

closed vessels in an atmosphere of nitrogen, whereby oxidation and hydrolysis are prevented. The solutions prepared under pressure from the exposed starch are sometimes cloudy and deposit a precipitate on centrifuging. Wheat starch is also peptized by ultraviolet light, and in this case the behavior of the solution on electrodialysis is the reverse of that of the unexposed starch. As with potato starch, a relatively simple organic acid containing phosphorus is found in the anode cell on electrodialysis.

The changes which take place when starch, glycogen, inulin, dextrin, amylose and amylopectin are irradiated with the quartz mercury lamp have been followed quantitatively by Lieben, Löwe and Bauminger²³⁷ in respect to lactic acid and reducing substance produced. The latter consists not merely of glucose but also of maltose and other reducing sugars, including traces of triose. Amylose and amylopectin are less affected than is starch.²³⁸

It is claimed by Tanret and Guillaume²³⁹ that 2-per cent solutions of glucosides (salicin, amygdalin, etc.) and also certain esters may be hydrolyzed by exposures to wave-lengths in the range 1800 to 3100A for three to twenty-four hour periods. An increase in temperature or acidity of the medium increases the rate. In the case of nine glucosides, the order of hydrolysis differed when the hydrolyzing agent was ultraviolet rays, acids, and enzymes.²⁴⁰ After twelve hours of irradiation, various glucosides were hydrolyzed to the following percents: helicin, 100 per cent, gentiopicrin, 59, coniferin, 55.4, amygdalin, 35.4, salicin, 31.1, picein, 23.3, arbutin, 13.4 and methylarbutin, 8.1 per cent. Floridoside (glyceryl α -galactoside) and α - and β -methylglucosides were hydrolyzed very slowly and xanthorhamnin not at all, although it absorbed the entire ultraviolet spectrum used. Acetylsalicylic acid, tropacocaine, homotropococaine, monobutyryn and asparagine were hydrolyzed more or less, but ethyl acetate, glycylglycine, *dl*-alanylglycine, glycytyrosine, and urea were not.²⁴¹ Saponin is claimed by Wolf²⁴² to lose its toxicity after irradiation by ultraviolet in solution, so that it may be used as an emulsifying agent in food products without danger of producing hemolysis.

²³⁷ Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z.*, **271**, 209 (1934).

²³⁸ See also Isemura, T., *J. Chem. Soc. Japan*, **56**, 772 (1935); *Chem. Abs.*, **29**, 7352 (1935).

²³⁹ Tanret, G., and Guillaume, A., *Compt. rend.*, **201**, 1057 (1935).

²⁴⁰ Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936); *Brit. Chem Abs.*, **1936A**, 572.

²⁴¹ Guillaume, A., and Tanret, G., *Compt. rend.*, **201**, 1057 (1935); *Bull. soc. chim. biol.*, **18**, 556 (1936); *Chem. Abs.*, **30**, 5503 (1936).

²⁴² Wolf, J., German Patent 524,892, June 3, 1927; *Chem. Abs.*, **25**, 4326 (1931).

Chapter 24

Acids and Other Aliphatic Compounds

The action of ultraviolet light on many organic acids or their salts leads to decomposition¹ of the latter, but in unsaturated acids the polymerizations and stereoisomeric transformations characteristic of the photochemical behavior of double bonds often occur.

Ley and Arends² showed that saturated mono- and di-carboxylic aliphatic acids, in vapor form, in hexane, or in aqueous solutions have an absorption band beginning at about 2400A, with a maximum at 2040-2070A. This maximum is ascribed to the carbonyl group, since it appears also in the chlorides and anhydrides of the acids. The nature of the absorption is not materially affected by ester formation, but is usually totally changed by salt formation. Sodium acetate, considered as typical of the salts of acetic acid, shows no maximum at 2040A, but continues to absorb the shorter wave-lengths with increasing intensity. The curve for formic acid lies somewhat nearer to the visible. Ramsperger and Porter³ found the bimolecular form of formic acid primarily responsible for the absorption between 2260 and 2500A. Harris⁴ believed the unimolecular form to agree in absorption with that of the other acids, having its maximum at 2050A.

Lederer⁵ finds some specific absorption by all fatty acids between 2700 and 2800A, that of propionic extending to 2700A and stearic to 2800A. A confirmation has been given by Hartleb,⁶ but the cause of this absorption has not yet been definitely established.

There is spectroscopic evidence for the formation of solvates of both esters and free acids in various solvents⁷ and Herold⁸ concludes from ultraviolet absorption measurements that the formation of solvates (hydrates or semiacetals) is a necessary preliminary to the dissociation of the fatty acids.

ACETIC ACID

In the photolysis of acetic acid in the absence of air, Berthelot and Gaudechon⁹ obtained a gas which contained 44 per cent of carbon dioxide, 17 per cent of carbon monoxide and 39 per cent of combustible gases. Farkas and Wansbrough-Jones¹⁰ find that undissociated formic, acetic and succinic acids in aqueous solution undergo several simultaneous photochemical changes. One is the direct formation of carbon dioxide and a hydrocarbon by a process analogous to that

¹ Kailan, A., *Monatsh*, **34**, 1209 (1913).

² Ley, H., and Arends, B., *Z. physik. Chem.*, **B4**, 234 (1929); **B17**, 177 (1932); Price, W. C., and Evans, W. M., *Proc. Roy. Soc.*, **A162**, 110 (1937); earlier observations are due to Hantzsch, A., and von Halban, H., *Z. Elektrochem.*, **29**, 221 (1923).

³ Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

⁴ Harris, L., *Nature*, **118**, 482 (1926).

⁵ Lederer, E. L., *Allgem. Öl- u. Fettstg.*, **27**, 237 (1930), *Chem. Abs.*, **25**, 2014 (1931).

⁶ Hartleb, O., *Strahlentherapie*, **39**, 442 (1931).

⁷ Ley, H., and Hunecke, H., *Ber.*, **59**, 510 (1926).

⁸ Herold, W., *Z. physik. Chem.*, **B18**, 265 (1932); *Z. Elektrochem.*, **38**, 633 (1932).

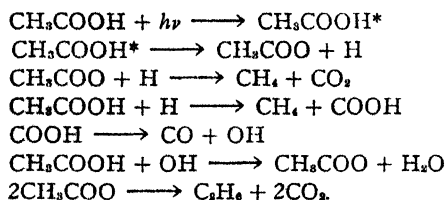
⁹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68 (1913); *J. Soc. Chem. Ind.*, **29**, 1081 (1911).

¹⁰ Farkas, L., and Wansbrough-Jones, O. H., *Z. physik. Chem.*, **B18**, 124 (1932).

encountered in the photochemistry of the ketones, $\text{RCOOH} + h\nu \rightarrow \text{CO}_2 + \text{RH}$. With acetic and propionic acids, the reaction, $\text{RCOOH}(\text{H}_2\text{O}) + h\nu \rightarrow \text{CO} + \text{H}_2\text{O} + \text{ROH}$ occurs (in aqueous solution) about 60 per cent as frequently as the reaction yielding carbon dioxide. Longer-chained acids tend, as do the aldehydes, to yield some unsaturated hydrocarbon and a shorter-chained acid: $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{COOH}$. All of the acids yield condensation products.

In acetic acid vapor, which shows only a continuous spectrum, the chief reaction is dissociation into carbon dioxide and methane. The quantum yield (1850-2300Å) is 0.45 for acetic acid, 1.0 for propionic acid and 0.4 for succinic acid. When polymers of the acids are present, the reaction is more complex. (See formic acid.) When acetic acid is decomposed in hexane solution, the solvent is attacked.

Burton,¹¹ using the mirror method, has found that hydrogen atoms but not methyl radicals are formed in the photolysis of acetic acid. Terenin¹² has also detected the hydroxyl radical in photolyses at about 1560Å. To account for these results, Burton suggested two possible mechanisms, one being:



In aqueous solutions of salts of aliphatic acids the decomposition is even more complex and, according to Jaeger and Berger,¹³ is dependent upon the acid anion and other ions which may be present, particularly cations. According to Farkas and Wansbrough-Jones, the reaction depends upon absorption within the electron affinity spectrum of the anion by the process: $\text{A}'(\text{H}_2\text{O}) + h\nu \rightarrow \text{A} + \text{OH}' + \text{H}$, but because of a subsequent reaction $\text{A} + \text{H} \rightarrow \text{A}' + \text{H}^+$, the yield of the decomposition products is small. Addition of alkali favors the evolution of hydrogen and the formation of acids of higher basicity. Farkas states¹⁴ the quantum yield of the reaction of the primarily produced hydrogen atom with acetate ion to form methane and carbon dioxide is 0.05 at pH 8.5. When silver acetate is used the hydrogen atoms may react with silver ions, so that the usual retarding process is less effective.

Acetic acid and aniline¹⁵ in equimolar proportions when exposed to ultraviolet rays for 24 hours give nearly a 100 per cent yield of acetanilide. Propionic and benzoic acids act similarly. The yield of propionanilide is about 65 per cent of theoretical and that of benzanilide considerably less. Amide formation occurs much less readily, ammonium acetate in the presence of excess ammonium hydroxide giving only about 5.3 per cent acetamide, and ammonium benzoate even less benzamide.

¹¹ Burton, M., *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936). Data for the photolysis of propionic acid have been given by Henkin, H., and Burton, M., *Ibid.*, **60**, 831 (1938). As in acetic acid, both hydrogen atoms and ultimate molecules are produced in primary processes. The relative number of hydrogen atoms per einstein is greater than in acetic acid.

¹² Terenin, A., *Acta Physicochim. U.R.S.S.*, **3**, 181 (1935).

¹³ Jaeger, F. M., and Berger, G., *J. Chem. Soc.*, **119**, 2070 (1921); *Proc. Roy. Soc.*, **23**, 84 (1920).

¹⁴ Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

¹⁵ Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922).

dl- α -Iodopropionic acid soon becomes colored by free iodine in daylight, and loses its iodine more rapidly in direct sunlight, or in chloroform solution in glass.¹⁶

FORMIC ACID¹⁷

Ramsperger and Porter¹⁸ accomplished the complete decomposition of formic acid vapor by exposing the acid for 16 hours at a distance of 20 cm. from a 220-volt mercury arc at 20°C. Carbon monoxide and water constituted 64 per cent, and carbon dioxide and hydrogen, 36 per cent, of the mixed products formed by two photolytic processes. Müller and Hentschel¹⁹ believed that some of the hydrogen formed reduces the acid further. Although the formation of methanol and formaldehyde could not be established, a noncrystalline solid was observed to form in the solution. They found also that the decomposition could be catalyzed by finely dispersed platinum.

Double molecules of formic acid present in the vapor phase decompose almost entirely to carbon dioxide and hydrogen.²⁰ The single molecules yield both these products and carbon monoxide and water, the ratio varying with the temperature and wave-length employed. At 40°C. and 2540Å, the ratio is approximately 75.5 per cent carbon monoxide and water to 24.5 per cent carbon dioxide and hydrogen. At 100°C. and with the same wave-length, the amounts are 69 and 31 per cent, respectively. At shorter wave-lengths, 2100 and 1900Å, the ratio is 42 per cent to 58 per cent. At these two latter wave-lengths, the quantum yield is unity for the decomposition of either double or single molecules.

An application of the para-hydrogen conversion test for atomic hydrogen showed only minimal formation of hydrogen atoms and carboxyl radicals, so that the primary process may consist in a rearrangement of bonds to give hydrogen and carbon dioxide directly. Burton²¹ was unable to detect hydrogen atoms by the mirror test. Terenin,²² however, detected OH by its emission spectrum when wave-lengths near 1560Å were used.

According to Allmand and Reeve,²³ radiation of wave-length 3100Å produces a slow decomposition of aqueous solutions of formic acid, the products being carbon dioxide and hydrogen, traces of formaldehyde and some more complex compound of highly reduced nature. The latter products were secured by reduction of formic acid by some of the hydrogen. In the presence of the uranyl ion, the decomposition in aqueous solutions is sensitized to visible light.²⁴ The velocity of photolysis depends upon the concentrations of the formic acid and the uranyl ion. With increasing concentrations of the latter, the velocity at first increases rapidly and passes through a maximum. The reaction is strongly desensitized by iodide, chloride and ferrous ions, hydroquinone, potassium dichromate, silver nitrate, sodium nitrite, potassium cyanide and mercuric sulfate, slightly desensitized by cupric sulfate, chromic sulfate,

¹⁶ Hannerz, E., *Ber.*, **59B**, 1367 (1926).

¹⁷ It has been claimed that methyl alcohol vapor and carbon monoxide exposed to ultraviolet rays or led over barium and potassium carbonates at 500°, give methyl formate and high-molecular compounds. Wietzel, G., and Wietzel, R., *German P.* 442,125, June 10, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* 1928B, 8.

¹⁸ Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

¹⁹ Müller, E., and Hentschel, H., *Ber.*, **59**, 1854 (1926).

²⁰ Gorin, E., and Taylor, H. S., *J. Am. Chem. Soc.*, **56**, 2042 (1934); see also Herr, W. N., and Noyes, W. A., Jr., *Ibid.*, **50**, 2345 (1928).

²¹ Burton, M., *J. Am. Chem. Soc.*, **58**, 1655 (1936).

²² Terenin, A., *Acta Physicochim. U.R.S.S.*, **3**, 181 (1935).

²³ Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, 2852 (1926).

²⁴ Ouellet, C., *Helv. Chim. Acta*, **14**, 936 (1931); *Chem. Abs.*, **26**, 656 (1932), Büchi, P. F., [*Z. physik. Chem.*, **111**, 269 (1924)] gives the quantum yield as 0.7.

sodium nitrate and potassium fluoride. Photolysis is not affected by trisodium phosphate, ammonium acetate or magnesium sulfate. Oxidation-reduction properties of the desensitizer, which remains unchanged, play an important part in its effect. Increased concentration of the formic acid diminishes the effect of a desensitizer, but at 25 per cent concentration the velocity becomes almost independent of the concentration. When the concentration of the desensitizer is increased, the desensitizing effect increases rapidly at the beginning and then more slowly. Ghosh and Mitter²⁵ have given spectroscopic evidence for the formation of intermediate compounds of uranyl salts and organic acids.

A reaction in aqueous solution between sodium formate and iodine studied by Dhar and Bhargava²⁶ is unimolecular in darkness and "semimolecular" in light. Its velocity is proportional to the 0.75 to 0.66 power of the intensity of the incident light. It is a chain reaction, the quantum yield varying from 26 to 64, increasing with temperature and frequency of the light. More light is absorbed by the mixture than by the reactants separately.

Attention has been called to the formation of a peroxide from formic acid in the presence of oxygen, by short ultraviolet rays. The peroxide was assumed by Cantieni²⁷ to be performic acid.²⁸

Relatively little work has been done on the photolysis of acetyl halides. The decomposition products contain carbon monoxide and the methyl halide, but no hydrogen, ethane or ethylene. The decomposition products from acetyl chloride contained hydrogen chloride and a polymer of either biacetyl or ketene. The products from acetyl bromide are bromine and $\text{CH}_2\text{BrCH}_2\text{Br}(\text{?})$. Iodine is formed from acetyl iodide.²⁹

The rates of decomposition of carbonyl hypohalites, e.g., $\text{C}_2\text{H}_5\text{COOBr}$, are dependent both upon concentration and illumination, according to Bockemüller and Hoffmann,³⁰ daylight greatly retarding the decomposition.

DIBASIC ACIDS

The photolysis of oxalic acid³¹ consists in a primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the formic acid into carbon monoxide and hydrogen by rays of short wave-length. Kailan³² concluded that the rate of the decomposition of dibasic acids increases with the duration of the exposure, but does not increase in proportion to the concentration of the acid. He found more carboxyl groups to be decomposed from malonic acid than from oxalic acid. Also, introduction of a hydroxyl group increased the rate of decomposition of dibasic acids. The rate of decomposition of malonic acid by sunlight in the presence of catalyst was found by Fay³³ to be exceedingly slow. Berthelot and Gaudechon³⁴ found uranyl salts to catalyze this

²⁵ Ghosh, J. C., and Mitter, B. N., *Quart. J. Indian Chem. Soc.*, **4**, 353 (1927); *Chem. Abs.*, **22**, 1899 (1928).

²⁶ Dhar, N. R., and Bhargava, P. N., *J. Phys. Chem.*, **39**, 1231 (1935).

²⁷ Cantieni, R., *Helv. Chim. Acta*, **19**, 1153 (1936); *Ber.*, **69B**, 1153 (1936). Similar behavior is shown by other fatty acids. *Z. wiss. Phot.*, **36**, 90 (1937); *Chem. Abs.*, **31**, 8381 (1937).

²⁸ Data on the decomposition of acetyl peroxide have been given by Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (1937).

²⁹ Etzler, D. H., and Rollefson, G. K., *J. Chem. Phys.*, **6**, 653 (1938).

³⁰ Bockemüller, W., and Hoffmann, F. W., *Ann.*, **520**, 165 (1935); *Chem. Abs.*, **29**, 7940 (1935).

³¹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **158**, 1791 (1914).

³² Kailan, A., *Monatsh.*, **34**, 1209 (1913).

³³ Fay, H., *Am. Chem. J.*, **18**, 269 (1896).

³⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 333 (1913).

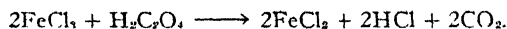
reaction, and Volmar³⁵ found the main products of decomposition to be acetic acid and carbon dioxide.

Volmar also subjected a series of dibasic acids in 0.01 molar solutions to the light of a quartz mercury arc. Oxalic and malonic acids yields formic and acetic acids, respectively. Succinic acid gave a trace of propionic acid, but glutaric acid gave no butyric acid and liberated only 0.13 cc. of carbon dioxide in four hours. Oxalic acid, like formic acid, has the maximum sensitivity of the corresponding series of acids and has an absorption maximum at 2500Å.³⁶ As the chain between the carboxyl groups lengthens, their mutual influence diminishes and from succinic acid onwards the groups behave as though they were independent.

Noyes and Kouperman³⁷ found a long induction period for the photolysis of solid oxalic acid by wave-lengths shorter than 2500Å. Following the induction period, the rate of decomposition attained a practically constant rate. This rate was apparently greater when short wave-lengths were employed. Their explanation was that such radiations might endow the decomposition products with an excess of kinetic energy which would aid their more rapid diffusion out from the interior of the crystals. The rate of thermal decomposition of solid silver oxalate may be increased by a previous exposure of the salt to light of wave-lengths less than 5200Å.³⁸

It was reported by Noyes and Kouperman that the rate of decomposition of oxalic acid was greater when the acid was in aqueous solution than when the acid was used alone. Allmand and Reeve³⁹ found the decomposition products of such solutions to be predominantly carbon dioxide, with small amounts of formaldehyde.⁴⁰ Wave-lengths as long as 3000Å were effective in causing photolysis. In all cases, the quantum yields were low, but appeared to increase on dilution of the solution. For a 0.68 molar solution, 100 quanta were absorbed per molecule decomposed at 2650Å, 2450 at 3000Å and 1060 at 3650Å.

Winther and Oxholt-Howe⁴¹ found the quantum sensitivity of the decomposition of iron oxalate, succinate, tartrate, citrate and acetate for short wave-lengths to be greater than unity. Kunz-Krause and Manicke⁴² reported that under the catalytic action of ferric chloride, 5.3 per cent of crystalline oxalic acid suffers decomposition after a five-hour arc light exposure and 61.7 per cent after 16 hours. Padoa and Vita⁴³ studied the action of light on the reaction



They believed that the sum of the effects obtained in the blue and violet regions is 1.123 times that of white light. In the presence of quinine bisulfate, the zone of active radiations was widened and the sum of the effects of blue, green and violet lights was said to be 2.125 times that of white light.

Complex Oxalate Ions. The quantities of potassium cobaltioxalate⁴⁴

³⁵ Volmar, *Compt. rend.*, **180**, 1172 (1925).

³⁶ See Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); Vlès, F., and Gex, M., *Compt. rend.*, **180**, 1342 (1923).

³⁷ Noyes, W. A., Jr., and Kouperman, A. B., *J. Am. Chem. Soc.*, **45**, 1398 (1923); Wobbe, D. E., and Noyes, W. A., Jr., *Ibid.*, **48**, 2856 (1926).

³⁸ Benton, A. F., and Cunningham, G. L., *J. Am. Chem. Soc.*, **57**, 2227 (1935).

³⁹ Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, 2834 (1926).

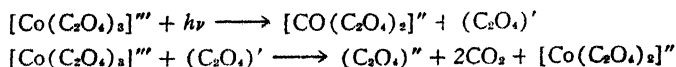
⁴⁰ Baur, E., believes there is a direct decomposition into carbon monoxide, carbon dioxide and water. *Z. physik. Chem.*, **111**, 315 (1924).

⁴¹ Winther, C., and Oxholt-Howe, H., *Z. wiss. Phot.*, **14**, 196 (1914).

⁴² Kunz-Krause, H., and Manicke, P., *Ber. Pharm. Ges.*, **32**, 209 (1922).

⁴³ Padoa, M., and Vita, N., *Gazz. chim. ital.*, **54**, 147 (1924); see also *Atti Cong. naz. chim. pura applicata*, 398 (1923).

decomposed by the mercury arc in quartz vessels in identical intervals of time were approximately independent of the initial concentrations and determined chiefly by the light energy absorbed. The addition of alcohol had no appreciable effect, but neutral salts did have marked effects. Bhagwat and Dhar,⁴⁵ found the reaction to be greatly accelerated by short wave-length radiation. Also, the latter investigators gave the temperature coefficient of the thermal reaction as 3.7. In incandescent light, the coefficient was 1.85 and in sunlight 1.13. In sunlight the velocity was proportional to the square root of the light intensity, but in lamp light it was directly proportional to the intensity. Murgulescu⁴⁶ also finds the decomposition of 0.02-0.002 molar potassium cobaltioxalate by light of wave-lengths 4360, 4050, 3660 and 3130A to be of zero order.



In most complex oxalates, Bhagwat⁴⁷ found the quantum yield to be two. He assumes the formation of an activated molecule as the primary process. On collision of this activated molecule with an unexcited molecule, both are decomposed. Potassium cuprioxalate requires a sensitizer in visible light. The decomposition products include copper, cuprous oxide, carbon monoxide and carbon dioxide. The quantum yield is 0.66. Bhagwat makes the assumption that the molecule absorbs two quanta before being further activated through the sensitizer. The sensitizers employed by Dube and Dhar⁴⁸ were ferric chloride or uranyl nitrate. The reaction was of zero order. Increasing the amount of the sensitizer increased the rate through a maximum. The reaction was more effectively retarded by oxygen than by carbon dioxide. It was accelerated by the presence of a large excess of potassium oxalate.

Potassium manganioxalate absorbs light throughout the visible, with a maximum at about 4870A. Ghosh and Kappanna⁴⁹ find white light to more than treble the velocity of thermal decomposition of the potassium complex. The quantum yield is one when plane polarized light is used. Addition of oxalic acid diminishes the velocity of the reaction.

Allmand and Webb⁵⁰ found in the photodecomposition of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, that the quantum yields, which decrease with increasing wave-length, are of the order of unity. The presence of potassium oxalate caused a slight decrease in the quantum yield, but all other electrolytes tested increased the yield slightly. Experiments with mixed light with varying proportions of two or three mercury arc lines, showed an amount of decomposition 25 to 30 per cent greater than that calculated on the basis of an additivity of their separate effects. On the other hand, the use of a continuous band between 3900 and 4600A caused a degree of decomposition about 20 per cent lower than that expected on the basis of additivity. The effects of intermittent and continuous exposures were the same. The quantum yield was independent of the intensity of the line 3650A (in some experi-

⁴⁴ Berger, G., *Rec. trav. chim.*, **44**, 47 (1925); Jaeger, M., and Berger, G., *Proc. K. Akad. Wetensch. Amsterdam*, **23**, 84 (1920); *J. Chem. Soc.*, **118**, ii, 725 (1920).

⁴⁵ Bhagwat, W. V., and Dhar, N. R., *Z. anorg. Chem.*, **197**, 18 (1931); *Brit. Chem. Abs.*, **1931A**, 579.

⁴⁶ Murgulescu, I. G., *Bul. soc. stiinte Cluj*, **8**, 193 (1935); *Chem. Abs.*, **30**, 4402 (1936).

⁴⁷ Bhagwat, W. V., *Z. anorg. allgem. Chem.*, **218**, 365 (1934); *Chem. Abs.*, **28**, 6636 (1934).

⁴⁸ Dube, H. L., and Dhar, N. R., *J. Phys. Chem.*, **36**, 626 (1932).

⁴⁹ Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3**, 127 (1926); *Brit. Chem. Abs.*, **A**, 1014 (1926).

⁵⁰ Allmand, A. J., and Webb, W. W., *J. Chem. Soc.*, 1518, 1531 (1929).

ments 4050A) over a range of fifteen to one, whether continuous or intermittent. These results tended to confirm the work of Padoa and Vita (see Chapter 12). They suggested that the primary result of the absorption of a light quantum is the activation of the ferrioxalate ion, a process regarded as involving the partial dislocation of the union between the ferric ion and one of the attached oxalate ions. Reaction then occurs on collision of such an activated ion with a normal ion. More recently, Allmand and Young⁵¹ confirmed the synergistic action of two monochromatic rays and showed that the temperature coefficient for this reaction is "negative." They also observed that in aqueous solutions, the velocity of the photoreduction of ferric chloride by oxalic acid is proportional to the intensity, that the ferric ion has no effect other than a slight light filter effect, and that the quantum efficiency is of the order of unity.⁵² Kornfeld and Mencke⁵³ had found the velocity proportional to the square root of the intensity of light in the blue, green, and violet and, within limits, independent of the concentration of the reagents. It varies with the duration of the reaction and rapidly tends to drop to zero. Addition of ferrous sulfate retards the reaction at a rate proportional to the concentration of the sulfate.

The decomposition of oxalic acid can also be sensitized to light by chromium and by uranyl salts, the latter being about three times as effective as the former.⁵⁴ The reaction in the presence of uranyl salts has been suggested for standardizing light sources employed in determination of the light fastness of dyes.⁵⁵ Büchi,⁵⁶ who finds the quantum yield to be unity, attributes the reaction to the decomposition of the non-ionized molecules of uranyl oxalate ($\text{UO}_2\text{C}_2\text{O}_4$) or of the complex ions ($\text{UO}_2(\text{C}_2\text{O}_4)_2$), since the rate is only independent of the oxalic acid concentration when the latter is equimolar with or greater than the uranyl salt.

Müller⁵⁷ disagrees with the theory of the formation of a sensitizer-complex molecule and attributes the decomposition to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. Pierce⁵⁸ confirmed Bruner and Kozak⁵⁹ and Bacon⁶⁰ in finding a temperature coefficient of unity, but was unable to decide between the mechanisms involving a sensitizer-complex and that of Müller. Pringsheim⁶¹ discards the theory of collisions with activated molecules because he finds the inhibiting effect of iodide ions on the photolysis too small in comparison with their effect on fluorescence. He therefore favors complex formation. The solution must not be alkaline when intended for use in an actinometer. The application of the reaction for this purpose has been discussed in Chapter 7, where more recent quantum yield measurements are mentioned.

The Eder Reaction. A reaction formerly employed in actinometry, but really too complex and too subject to the presence of accelerating and inhibiting impu-

⁵¹ Allmand, A. J., and Young, K. W., *J. Chem. Soc.*, 3079 (1931).

⁵² See also Baur, E., Ouellet, C., and Wackerlin, E., *Z. wiss. Phot.*, 30, 88 (1931); *Chem. Abs.*, 26, 3729 (1932).

⁵³ Kornfeld, G., and Mencke, E., *Z. Elektrochem.*, 34, 598 (1928).

⁵⁴ Landau, M., *Compt. rend.*, 156, 1894 (1913); Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, 17, 211 (1913); Boll, *J. Chem. Soc.*, 108, ii, 123 (1925); Kunz-Krause, H., and Manicke, P., *Ber. pharm. Ges.*, 32, 209 (1922); Sandonini, C., *Atti accad. Lincei*, 2, 427 (1925); *Chem. Abs.*, 20, 1018 (1926).

⁵⁵ Holmes, W. C., *Amer. Dyestuff Rep.*, 13, 188, 197 (1924); *Chem. Abs.*, 18, 1614 (1924).

⁵⁶ Büchi, P. F., *Z. physik. Chem.*, 111, 269 (1924); *Chem. Abs.*, 19, 1097 (1925); Baur, E., *Z. physik. Chem.*, 111, 315 (1924).

⁵⁷ Müller, R. H., *Proc. Roy. Soc.*, 121A, 313 (1929).

⁵⁸ Pierce, W. C., *J. Am. Chem. Soc.*, 51, 2731 (1929).

⁵⁹ Bruner, L., and Kozak, J., *Z. Elektrochem.*, 17, 355 (1911).

⁶⁰ Bacon, R. E., *Philippine J. Sci.*, 2, 129 (1907); 5, 281 (1910).

⁶¹ Pringsheim, P., *Physica*, 4, 733 (1937); *Chem. Abs.*, 31, 8380 (1937).

rities, is the Eder reaction.⁶² A solution containing mercuric chloride and ammonium oxalate is employed. On exposure to light, the decomposition products of the oxalate were thought to bring about the reduction of the mercury salt to calomel. Winther⁶³ found that the sensitiveness of the solution to visible light depended upon the presence of traces of a ferric salt. The rate of deposition of calomel was proportional to the iron content provided this did not exceed a very low value. An excess of ferric salt, however, retarded the reaction, particularly in the absence of dissolved oxygen. Furthermore, highly purified solutions were still decomposed by ultraviolet light, although not markedly by visible light.

Comparative experiments by Winther and Oxholt-Howe,⁶⁴ in which equal volumes of the filtrate from the calomel formed in a previous exposure and a fresh solution of the same composition were exposed to the influence of light under similar conditions, indicate that the initial photochemical action leads to the formation of some substance which acts as a powerful negative catalyst. This is also observed in the case of a purified Eder's solution to which eosin has been added as a sensitizer to the visible. In general, the effect becomes more marked as the intensity of the light increases. There is an appreciable loss of sensitivity if the eosin solution has been insolated before having been added to the Eder's solution. Velocity measurements of these reactions have been made by Shpol'skii and Ivanova.⁶⁵

Padoa and Minganti⁶⁶ have measured the temperature coefficients of the reaction at various wave-lengths. The reaction in green light was very slow and a small proportion of a dilute aqueous solution of tetrabromofluorescein was added as a sensitizer; the latter was also employed in some experiments with white light. The results were as follows: white light, 1.29; ultraviolet, 1.05; dark blue, 1.21; green with sensitizer, 1.75; white light with sensitizer, 1.50. Here it is apparent that the longer the wave-length, the higher the temperature coefficient. The effect of the sensitizer in raising the temperature coefficient with white light is attributed to the fact that the sensitizer gives preponderance to the action of the yellow and green rays, which have little activity when no sensitizing agent is present.

Trifonov⁶⁷ found that potassium mercuric oxalate can be decomposed by water and by light. Various workers, including Ghosh and Rangcharya,⁶⁸ have advanced evidence, in some cases spectrographic, for the formation of an intermediate compound in Eder's solution. Cartledge and Djang⁶⁹ find cobaltous salts alone to be much less effective in inducing the reaction than are ferrous salts. The former affect chiefly the dark reaction. The effect of the cobaltioxalate complex ion is essentially a pure catalysis in the light. The inhibiting effect of oxygen

⁶² Krauss, F., and Berge, K., *J. Prakt. Chem.*, **136**, 257 (1933); see also Bekhterev, P., *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925); *Chem. Abs.*, **20**, 2459 (1926); Pitzer, E. C., Gordon, N., and Wilson, D., *J. Am. Chem. Soc.*, **58**, 67 (1936); Wieland, H., and Zilg, W., *Annalen*, **530**, 1656 (1937); *Chem. Abs.*, **32**, 1656 (1938).

⁶³ Winther, C., *Z. wiss. Phot.*, **8**, 135, 197 (1910); **14**, 172 (1914); Beiger, G., *Rec. trav. chim.*, **40**, 387 (1921); *Chem. Abs.*, **16**, 1175 (1922).

⁶⁴ Winther, C., and Oxholt-Howe, H., *Z. wiss. Phot.*, **13**, 89 (1913); *J. Chem. Soc.*, **106**, II, 10 (1914).

⁶⁵ Shpol'skii, E., and Ivanova, E. N., *J. Phys. Chem. (U.S.S.R.)*, **6**, 133 (1935); *Nature*, **16**, 647 (1930); *Chem. Abs.*, **29**, 7809 (1935). For the effect of oxygen, see Shpol'skii, E., and Il'ina, A., *Acta Physicochim. U.R.S.S.*, **3**, 269 (1935); *Brit. Chem. Abs.*, **A**, 1214 (1936).

⁶⁶ Padoa, M., and Minganti, T., *Atti accad. Lincei*, **24** (V), ii, 97 (1915); *J. Chem. Soc.*, **108**, (ii), 719 (1915).

⁶⁷ Trifonov, N., *Mit. wiss.-tech. Arb. Republ. (Russ.)*, **13**, 72 (1924); *Chem. Zentr.*, 382 (1925).

⁶⁸ Ghosh, J. C., and Rangcharya, T. L. K., *J. Indian Chem. Soc.*, **5**, 569 (1928).

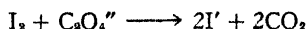
⁶⁹ Cartledge, G. H., and Djang, T. G., *J. Am. Chem. Soc.*, **55**, 3214 (1933).

is greatest with the catalyzed photolysis, less with that which is uncatalyzed and least on the photolysis of the cobaltioxalate ion alone.⁷⁰

Air, oxygen, hydrogen peroxide and ozone each inhibit the Eder reaction when the latter is carried out in the light of the carbon arc.⁷¹ The same is true of the reduction of ferric oxalate. Roseveare and Olson⁷² and Oberhauser and Schormüller⁷³ consider the Eder reaction a chain reaction. Phenols also strongly depress the reaction, an effect attributed by Weber⁷⁴ to a deactivation of the activated molecules or ions which form in the primary process. The same is true also of the eosin-sensitized reaction. When the solutions are saturated with oxygen, however, the phenols can depress the reaction only by acting as internal filters. Weber also believes the photosensitive component of the (unsensitized) solution to be a complex compound.

In the presence of eosin and with approximately monochromatic light of wavelength 5200A, 5460 or 5760A, there is a short induction period, after which the reaction proceeds linearly with time.⁷⁵ The speed of reaction is proportional to the intensity of light, both in the case of white light and of monochromatic illumination. In the concentration interval 5×10^{-7} to 5×10^{-5} gm. per cc., the speed increases in proportion to the concentration, but between 3×10^{-5} and 10^{-4} gm. per cc. the speed is constant. At higher concentrations, the rate begins to decrease. The decrease of sensitization as well as the damping of fluorescence as functions of the concentration begin from the same sharp threshold. The rate of the reaction is proportional to the concentration of mercuric chloride and, above concentrations of 0.01 gm. per cc., is independent of the concentration of oxalate. Between 15° and 5°, the temperature coefficient is 2.6 and between 25° and 15°, 1.9. The energy of activation is between 10 and 15 kcal. Beginning at 30°, the dark reaction acquires a noticeable speed. For the wave-lengths 5470 and 5760A, the quantum yield was, in the presence of oxygen, 12.5, a correction being made for the energy lost as fluorescence.⁷⁶

Reaction Between Iodine and Potassium Oxalate in Aqueous Solution. The photochemical reaction between iodine and potassium oxalate



has been the subject of much study.⁷⁷ Berthoud and Bellenot showed that the rate of reaction is proportional to the concentration of the oxalate ion and inversely to the concentration of the iodide ion. The latter exerts a retarding effect. The rate is also proportional to the square root of the light intensity and to a power of the titratable iodine concentration which varies between 0.5 and -0.5 depending upon the completeness of the absorption of the light, that is, upon the wave-length. When absorption is weak, as it is when red light is employed, the rate is directly proportional to the square root of the iodine concentration but when

⁷⁰ Cartledge, G. H., and Goldheim, S. L., *J. Am. Chem. Soc.*, **55**, 3583 (1933) have attempted a determination of the nature of the complexes formed in Eder's solution.

⁷¹ Dunncliff, H. B., and Joshi, J. N., *J. Indian Chem. Soc.*, **6**, 121 (1929); *Chem. Abs.*, **23**, 2887 (1929).

⁷² Roseveare, W. E., and Olson, A. R., *J. Am. Chem. Soc.*, **51**, 1716 (1929); **52**, 2617 (1930).

⁷³ Oberhauser, F., and Schormüller, J., *Annalen*, **470**, 111 (1929).

⁷⁴ Weber, K., *Z. physik. Chem.*, **A169**, 224 (1934).

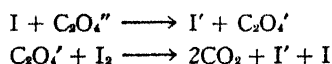
⁷⁵ Shpol'skiĭ, E. V., and Kolesnikova, N. I., *J. Phys. Chem. (U.S.S.R.)*, **5**, 1199 (1934); *Chem. Abs.*, **29**, 6145 (1935); *Brit. Chem. Abs.*, **A**, 809 (1936).

⁷⁶ For an analogous reaction between mercuric chloride and malic acid in the presence of various sensitizers, see Baur, E., *Helv. Chim. Acta*, **20**, 974 (1937).

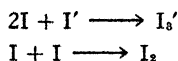
⁷⁷ Mukerji, B. K., and Dhar, N. R., *Z. physik. Chem.*, **120**, 75 (1926); *Z. Elektrochem.*, **31**, 621 (1925); *Trans. Faraday Soc.*, **21**, 489 (1926); Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 304 (1924); *J. Chim. Phys.*, **21**, 308 (1924).

absorption is complete as in blue light, the rate is inversely proportional to the square root of the iodine concentration. The results of Berthoud and Bellenot on the relation of the rate to the intensity were subsequently confirmed by others, who varied the intensity by more adequate methods than their sector device.⁷⁸ Bhagwat⁷⁹ believes this square root relation is not constant when the rate is varied over wide limits. Dhar, Bhattacharya and Mukerji⁸⁰ find the relation between the velocity and the light intensity to vary from one-third to approximately five-fourths when the wave-lengths employed are in the range 3340 to 8750 Å.

Berthoud and Bellenot accounted for their results in either red or blue light by a mechanism which involved the assumption that light dissociates iodine molecules but not the triiodide ion predominantly present in the solutions, which contained an excess of potassium iodide. Their mechanism involved the chain reactions



and the chain-breaking reactions



From these reactions and the assumption of stationary states for the concentrations of iodine atoms and $\text{C}_2\text{O}_4'$, it was possible to attain agreement with the experimental results for the reaction rates under varied conditions. They found quantum yields of 0.11 (4860 Å) with respect to the total energy absorbed or 3.2 with respect to that absorbed by I_2 . With blue light larger values, quantum yields up to 25 were obtained, verifying the chain nature of the reaction.

The temperature coefficients determined by Allmand and Young and by the Indian workers were high, about 3.0; those of the thermal reaction were as high as 6.86. This indicated a high energy of activation for some partial process, a feature difficult to reconcile with the chains proposed by Berthoud and Bellenot. Other reactions of iodine solutions required the concept that the triiodide ion present is photochemically decomposed with the production of iodine atoms and possibly the hypothetical ion I_2' . It was found possible by Dickinson and Ravitz⁸¹ to derive a mechanism from this concept of the primary process which also led to the experimental results of Berthoud and Bellenot. Such a mechanism was employed by Allmand and Young, who appended to their paper a discussion of the application of the mechanism to other photochemical oxidations by iodine. This mechanism has also been used by Griffith, McKeown and Winn⁸² in their treatment of the analogous reactions between bromine and potassium oxalate. They conceived the action of the free halogen to be only that of an internal light filter. In their experimental work they considered also the case in which there is but little of the iodide ion in excess. Berthoud,⁸³ however, has reiterated that it is the iodine molecule which is dissociated.

⁷⁸ Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, **129**, 562 (1926); Allmand, A. J., and Young, K. W., *Trans. Faraday Soc.*, **27**, 515 (1931).

⁷⁹ Bhagwat, W. V., *J. Indian Chem. Soc.*, **10**, 649 (1933), *Brit. Chem. Abs.*, **1934A**, 156; *Chem. Abs.*, **28**, 1928 (1934).

⁸⁰ Dhar, N. R., Bhattacharya, A. K., and Mukerji, B., *Nature*, **131**, 840 (1933); *J. Indian Chem. Soc.*, **12**, 151 (1935); *Brit. Chem. Abs.*, **1935A**, 832; *Chem. Abs.*, **29**, 5351 (1935).

⁸¹ Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52**, 4770 (1930).

⁸² Griffith, R. O., McKeown, A., and Winn, A. G., *Trans. Faraday Soc.*, **29**, 369, 386 (1933).

⁸³ Berthoud, A., *Helv. Chim. Acta*, **16**, 393 (1933).

Abel and Schmidt⁸⁴ have found evidence for the occurrence of the intermediary compound, probably C_2O_4' , the existence of which had been assumed in the earlier mechanisms and for which kinetic evidence had been given by Abel, Schmidt and Retter.⁸⁵ Its long life is indicated by an initial reaction rate increase and by the photochemical after-effect which had been studied by the intermittent sector method by Berthoud. (See Chapter 15.)

It may also be noted that Bhattacharya and Dhar⁸⁶ have proposed that the analogous bromine-oxalate reaction may proceed by way of excited molecules, since they believe it can be markedly accelerated by wave-lengths in the region of 7304A.

Malonic and Other Acids. The products of the photodecomposition of malonic acid, either in the presence or absence of uranyl sulfate, are acetic acid and carbon dioxide.⁸⁷ With 0.01 molar uranyl sulfate, the rate decreases with decreasing concentrations of malonic acid, being approximately proportional to the cube root of the concentration of the latter. In the absence of catalyst, the quantum yield varies between 0.68 and 0.81, being little affected by the wave-length. In the presence of catalyst it is lower, 0.27. The extent of ionization of the malonic acid does not affect the results. There may be two independent reactions, one due to the light absorbed by the malonic acid and the other to that absorbed by the catalyst, but there is no evidence for the formation of a complex between malonic acid and uranyl salts. The mechanism of the catalyzed reaction may involve the deactivation of excited uranyl sulfate molecules by collision with other uranyl sulfate or with malonic acid molecules. The temperature coefficient of the sensitized reaction is 1.13,⁸⁸ and that of the unsensitized reaction, 1.07.⁸⁹ Malonic anhydride (carbon suboxide, C_2O_3) is not appreciably affected by ultraviolet light.⁹⁰

Coster and van der Ziel⁹¹ have noted in the photochemical decomposition of monoalkylmalonic acids the formation of a substance that is not a fatty acid. This conclusion was drawn from study of its x-ray spectrum.

A uranyl salt-photosensitized reaction between succinic acid and methylene blue at 3600A is, after an initial induction period, of zero order with respect to the methylene blue. The rate is proportional to the incident intensity and independent of the pH. One-half of the collisions between excited uranyl ions and succinic acid molecules are believed to be effective.⁹²

Sattler and Nicolet⁹³ find treatment of diethyl cyclopropane-1,1-dicarboxylate with bromine at 40° to 50°C. under mercury arc irradiation through quartz gives both $Br < \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} > C(COOC_2H_5)_2$ and $BrCH_2 \cdot CH_2 \cdot CBr \cdot (COOC_2H_5)_2$, with relatively larger amounts of the latter than when no irradiation is used. Stoermer

⁸⁴ Abel, E., and Schmidt, H., *Naturwiss.*, **23**, 501 (1935).

⁸⁵ Abel, E., Schmidt, H., and Retter, K., *Z. physik. Chem.*, **163A**, 53 (1932); see also for the after-effect in the reaction between iodine and oxalic acid, Abel, E., Jokisch, R., Larisch, L., and Sassmann, H., *Z. Elektrochem.*, **43**, 629 (1937).

⁸⁶ Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **6**, 523 (1929); *Chem. Abs.*, **24**, 1033 (1930); Bhattacharya, A. K., Prakash, O., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931); **209**, 139 (1932).

⁸⁷ Pierce, W. C., Leviton, A., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **51**, 80 (1929).

⁸⁸ Pierce, W. C., *J. Am. Chem. Soc.*, **51**, 2731 (1929).

⁸⁹ Pierce, W. C., and Morey, G. H., *J. Am. Chem. Soc.*, **54**, 467 (1932).

⁹⁰ Edwards, M. J., and Williams, J. M., *J. Chem. Soc.*, 856 (1927).

⁹¹ Coster, D., and van der Ziel, A., *Z. physik. Chem.*, **B20**, 385 (1933).

⁹² Ghosh, J. C., Banerjee, T., and Bhatta, B., *Z. physik. Chem.*, **B32**, 163 (1936).

⁹³ Sattler, L., and Nicolet, B. H., *J. Am. Chem. Soc.*, **49**, 2066 (1927).

and Ladewig⁹⁴ discovered that when alcoholic solutions of *trans*-cyclopentane-1,2-dicarboxylic acid are exposed to the Uviol lamp, conversion into mono- and di-esters occurs. The expected transformation into the *cis* modifications did not take place.

Oxalyl chloride is slowly decomposed when irradiated with wave-lengths shorter than 3800A, the reaction being predominantly monomolecular with a low quantum yield.⁹⁵ The final products are phosgene and carbon monoxide, but it is believed that the initial products are chlorine and carbon monoxide. Two mechanisms are proposed for the effects of different wave-lengths. With short ones, the molecule breaks at the carbon-carbon bond, but with longer wave-lengths, a break at one of the carbon-chlorine bonds predominates.

HYDROXYLIC ACIDS

Volmar⁹⁶ found that hydroxy-acids and their salts undergo photolysis under the influence of ultraviolet rays, and to a lesser extent in sunlight. Tartaric acid in 1-per cent solution after three hours gave 3.5 cc. of gas composed of carbon dioxide 66 per cent, carbon monoxide 10 per cent, hydrogen 21 per cent, and hydrocarbons 3 per cent. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In the presence of alkalis, the carbon monoxide was lessened or absent, owing to condensation with a portion of the hydrogen with production of the aldehydic substances. The homologs of tartaric acid behaved similarly. The decomposition may be accelerated by the presence of catalysts such as uranyl acetate or iron salts.⁹⁷

Winther⁹⁸ finds the oxidation of citric, tartaric, lactic and oxalic acids to be insensitive to light.

In the presence of tartaric, lactic or mandelic acids as oxygen acceptors, the photochemical reduction of ferric chloride is of zero order.⁹⁹ With both mandelic acid and lactic acid, the life period of the excited ferric ion is of the order of 10⁻⁹ second. With tartaric acid, the reaction is complicated by the circumstance that the immediate product of the photooxidation of the acid also reacts with ferric salts under the influence of light. In the case of mandelic acid, the quantum yield is unity at 4880A, but becomes nearly 1.4 at 3900A; with tartaric acid and lactic acid, it is nearly 0.5 at 4880A and 0.8 at 3900A. Oxygen has been found a negative catalyst in the photochemical oxidation of lactic acid by bromine water by Dunnichiff and Joshi.¹⁰⁰

Lactic Acid. The decomposition of solid calcium lactate by ultraviolet light was found to give carbon monoxide, methane, ethane and hydrogen.¹⁰¹ Baudisch¹⁰² stated that lactic acid, repeatedly purified from its zinc salt, gave decisive reactions for acetaldehyde after about forty hours of irradiation followed by distillation. He could not detect methane, although Schanz had previously found

⁹⁴ Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).

⁹⁵ Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58**, 443 (1936).

⁹⁶ Volmar, *Compt. rend.*, **176**, 742 (1923); *J. Chem. Soc.*, **124**, (II), 279 (1923); *J. S. C. I.*, **42A**, 423 (1923).

⁹⁷ Neuberg, C., *Biochem. Z.*, **39**, 158 (1912).

⁹⁸ Winther, C., *Z. physik. Chem.*, **A174**, 41 (1935).

⁹⁹ Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **6**, 827 (1929); *Chem. Abs.*, **24**, 2055 (1930).

¹⁰⁰ Dunnichiff, H. B., and Joshi, J. N., *J. Indian Chem. Soc.*, **6**, 121 (1929); *Chem. Abs.*, **23**, 2887 (1929).

¹⁰¹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

¹⁰² Baudisch, O., *Biochem. Z.*, **103**, 59 (1920); *Chem. Abs.*, **14**, 2776 (1920).

a small amount.¹⁰³ Euler¹⁰⁴ had, however, previously shown that in pure aqueous solutions at 70°C., there were produced alcohol and a gas, the latter being 90 per cent carbon dioxide and 10 per cent a mixture of hydrogen and carbon monoxide. The rate did not appear to depend upon the concentration of the acid. An induction period of about two hours was noted. The rate of evolution of gas was not accelerated by the presence of either ferrous or ferric salts, although the latter were reduced.¹⁰⁵

Bredig, Mangold and Williams¹⁰⁶ state that inactive lactic acid is decomposed by light of wave lengths 2200 to 3000Å, but is not rendered optically active. Bolin¹⁰⁷ found that no decomposition occurs in glass flasks.¹⁰⁸ Burns¹⁰⁹ found wave lengths less than 2500Å effective in decomposing lactic acid in aqueous solution, the chief products being alcohol and carbon dioxide. The amounts of alcohol were 19 per cent in excess of those required by the assumption that the products are equal amounts of alcohol and carbon dioxide. The quantum yield, based on the carbon dioxide, was approximately 0.65, although the intensity measurements were admittedly inaccurate. Based upon the alcohol formed, it was 0.77. Carbon monoxide, 3.82 per cent of the total gas, saturated hydrocarbons, 5.36 per cent and unsaturated hydrocarbons 0.89 per cent, formed about 9 per cent of the gaseous products, but neither aldehyde nor hydrogen peroxide could be detected. Lieben, Löwe, and Bauminger¹¹⁰ have stated that lactic acid in alkaline solutions yields acetaldehyde and acetic acid, possibly formed through pyruvic acid, which in alkaline solution they found to be more readily attacked than lactic acid. The reaction could be sensitized to diffused daylight by sodium anthraquinonesulfonate. Müller¹¹¹ found that in the presence of uranyl sulfate, lactic acid and sodium lactate could be photochemically converted into acetaldehyde with a quantum yield of approximately unity (4025Å).

Ganassini¹¹² and Cianician and Silber¹¹³ found that lactic acid on prolonged exposure to sunlight in the presence of air yielded qualitative tests for acetic acid, pyruvic acid, acetaldehyde and carbon dioxide. Burns,¹¹⁴ in extending his work to oxygen-containing solutions, noted the chief products to be carbon dioxide, acetaldehyde, a peroxide and acetic acid, thus confirming the results of Baudisch and of Neuberg if it were assumed that they had worked without excluding oxygen. Neither ethanol nor pyruvic acid could be detected.

Studies of the rate of the oxidation of mandelic acid by methylene blue in the presence of uranyl nitrate as photosensitizer have been made by Ghosh, Narayanmurti and Roy¹¹⁵ at 4360, 3660, 3130 and 2540Å. In each case, there were short induction periods, those at 3660Å, and particularly 4360Å, being longer. The results

¹⁰³ Schanz, F., *Arch. ges. Physiol.*, **170**, 650 (1918).

¹⁰⁴ Euler, H., *Arkiv. Kem. Min. Geol.*, No 8, 1911; *J. Chem. Soc.*, **102**, ii, 112 (1912). Euler, H., and Ryd, S., *Biochem. Z.*, **51**, 97 (1913); Euler, H., and Lindberg, E., *Ibid.*, **39**, 410 (1912).

¹⁰⁵ See also Schanz, F., *Arch. ges. Physiol.*, **170**, 650 (1918).

¹⁰⁶ Bredig, G., Mangold, P., and Williams, T. G., *Z. angew. Chem.*, **36**, 456 (1923), *Chem. Abs.*, **17**, 3868 (1923).

¹⁰⁷ Bolin, I., *Z. physik. Chem.*, **87**, 490 (1914).

¹⁰⁸ For absorption data, see Dietzel, R., and Krug, R., *Arch. Pharm.*, **264**, 117 (1926).

¹⁰⁹ Burns, G. R., *J. Am. Chem. Soc.*, **51**, 3165 (1929).

¹¹⁰ Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z.*, **271**, 209 (1934).

¹¹¹ Müller, R. H., *Biochem. Z.*, **178**, 77 (1926).

¹¹² Ganassini, D., *Chem. Zentr.*, **I**, 387 (1913); **I**, 729 (1910); *Chem. Abs.*, **5**, 3236 (1911) from *Seduta soc. med. chir., Pavia*, 1909.

¹¹³ Cianician, G., and Silber, P., *Ber.*, **46**, 1558 (1913).

¹¹⁴ Burns, G. R., *J. Am. Chem. Soc.*, **52**, 5272 (1930).

¹¹⁵ Ghosh, J. C., Narayanmurti, D. S., and Roy, N. K., *Z. physik. Chem.*, **B29**, 236 (1935).

are complex. The photochemical oxidation of mandelic acid by bromine is of first order in the absence of potassium bromide and of zero order in its presence.¹¹⁶

Ghosh and Bhattacharya¹¹⁷ find that for monochromatic light, the rate constant is proportional to the square root of the absorbed energy. It was believed that the combined action of rays of two wave-lengths was less than that of the sum of their effects taken separately. For 4360A the quantum yield is 12.5, but it varies greatly with the light intensity and wave-length.

Ghosh and Ray¹¹⁸ find the uranyl-sensitized oxidation of mandelic acid by bromine a chain reaction with high quantum yield.

Tartaric Acid. The formation of reducing substances and carbon dioxide when tartaric acid is exposed to ultraviolet rays was described by Euler and Ryd.¹¹⁹ Ferric salts increase the rate of gas evolution, being themselves reduced.¹²⁰ In the presence of uranium salts, the α -hydroxy acids decompose slowly in sunlight into formic acid and the respective aldehydes and ketones.¹²¹ Tartaric acid yields glyoxal and citric acid yields acetone. This photochemical reaction could be employed for the detection of tartaric acid in a solution of citric acid. It appeared specific in that it was not given by any of the other aliphatic hydroxy-acids examined by Pavolino. After the addition of a uranium salt, the solution to be examined is exposed for at least thirty minutes to sunlight or to a light source of similar intensity. A few drops of phenylhydrazine or a corresponding quantity of a 5 per cent solution of its acetate are added. If tartaric acid was originally present, a yellow precipitate of phenylglyoxal osazone formed. Its color soon changed to wine red, probably because of the oxidative effect of the uranium salt.

Volmar¹²² finds that solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper and iron undergo decomposition on exposure to ultraviolet radiation with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. Potassium borotartarate is an exception; Volmer considers this due to the fact that it appears to be a mixture rather than a definite compound.

Light accelerates the direct air oxidation of sodium tartrate catalyzed by sodium sulfite, cerium hydroxide, sodium hydroxide, sodium carbonate or bicarbonate and ferrous hydroxide.¹²³

The oxidation of citric acid by chromic acid has temperature coefficients of 3.8 in darkness and 1.05 in light. The velocity varies as the square root of the light intensity, although in the case of tartaric and lactic acids, the rate is directly proportional to the light intensity.¹²⁴

In the case of citric acid, the process involves chains, the length of which increases with temperature and concentration.

¹¹⁶ Ghosh, J. C., and Purkayastha, R. M., *Z. physik. Chem.*, **7B**, 285 (1930); *J. Indian Chem. Soc.*, **6**, 361 (1929).

¹¹⁷ Ghosh, J. C., and Bhattacharya, S. K., *Z. physik. Chem.*, **31B**, 420 (1936).

¹¹⁸ Ghosh, J. C., and Ray, B. B., *Z. physik. Chem.*, **32B**, 158 (1936).

¹¹⁹ Euler, H., and Ryd, S., *Biochem. Z.*, **51**, 97 (1913).

¹²⁰ For data on the absorption spectra of tartaric acid solutions, see Bruhat, G., and Legris, R., *Compt. rend.*, **189**, 745 (1929); *Ann. Phys.*, **13**, 6 (1930); Descamps, R., *Compt. rend.*, **185**, 116 (1927); Lucas, R., and Schwob, M., *Compt. rend.*, **192**, 225 (1931); Bruhat, G., *Compt. rend.*, **192**, 489 (1931).

¹²¹ Pavolino, T., *Giorn. farm. chim.*, **79**, 310 (1930); *Chem. Abs.*, **25**, 251 (1931).

¹²² Volmar, *Compt. rend.*, **176**, 1465 (1923); *J. Chem. Soc.*, **124** (ii), 453 (1923).

¹²³ Palit, C. C., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 471 (1934); *Chem. Abs.*, **28**, 6780 (1934).

¹²⁴ Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **169**, 381 (1928); *Chem. Abs.*, **22**, 2111 (1928); *Z. anorg. allgem. Chem.*, **196**, 26 (1931); *Chem. Abs.*, **25**, 2052 (1931).

KETO-ACIDS

Comparatively few photochemical studies have been made of the ketonic acids, although occasional use has been made of ultraviolet absorption studies in the solution of problems relating to their constitution.¹²⁵

The yield of acetoin formed by ultraviolet light from aqueous solutions of pyruvic acid decreases from 100 per cent at 0.2 to 3 molar to 12 per cent at 11.4 molar.¹²⁶ In the presence of benzaldehyde, Discherl detected the formation of acetylphenylcarbinol. Benzaldehyde, benzene, salts and dehydrating agents hinder acyloin formation. The irradiation of 0.5 to 2 molar solutions of α -ketovaleric acid gave a 39 to 40 per cent yield of butyrolin.

The photooxidation of pyruvic acid is sensitized by eosin and isochlorophylline, slightly by rhodamine B and is inhibited by hydrogen cyanide. In alkaline solutions, oxalic acid is formed.¹²⁷ Lipmann¹²⁸ finds light to increase the reduction of methylene blue or of ferric ion by pyruvic acid. In the latter case, the pyruvic acid appeared to be oxidized to acetic acid and carbon dioxide.

When sensitized by eosin, chlorophyll, ferric or uranyl salts, the photochemical oxidation of glycolic acid yields formaldehyde and carbon dioxide, but glyoxylic acid gives only carbonic acid.¹²⁹ Ferric gluconate is reduced in sunlight to a ferrous salt.¹³⁰

HALOGENATED ACIDS

Ultraviolet light splits aqueous solutions of halogenated fatty acids and their salts in various ways, among the products being formaldehyde, carbon dioxide, hydrogen, and chlorine.¹³¹ Euler¹³² found that the haloacetic acids split off their halogen in aqueous solutions at 18°C. in ultraviolet light at a rate comparable to that in darkness at 100°C. The rate decreased at higher concentrations of the acids.

In benzene solution, monochloroacetic acid also lost some chlorine. Other products identified included a small amount of polyglycolide, fumaric acid and another unsaturated acid. Bromoacetic acid suffered decomposition more readily. Little is known of the mechanism by which the unsaturated acids were produced. In ether, qualitatively similar results were also reported with both monochloro- and monobromoacetic acids. The reaction becomes evident when wave-lengths between 3130 and 2660Å are employed. A quantum yield of unity at 2536Å was reported by Rudberg¹³³ for monochloroacetic acid. For monobromoacetic acid, he found it only 0.34, but that this increased as the solution was made alkaline. More recently, Farkas¹³⁴ has reported for monochloroacetic acid a quantum yield of 0.9, inde-

¹²⁵ Pyruvic acid, Henri V., and Fromageot, C., *Bull. soc. chim.*, **37**, 845 (1925); Pascal, P., *Ibid.*, **39**, 396 (1926); Benzylmethylglyoxal, Lowry, T. M., Moureau, H., and MacConkey, C. A., *J. Chem. Soc.*, 3167 (1928); Levulinic acid, Gex, M., *Arch. phys. biol.*, **10**, 250 (1933); α -ketonic acids, Fromageot, C., Pelletier, M., and Ehrenstein, P., *Bull. soc. chim.*, **51**, 1282 (1932); β -ketogluconic acid, Niederhoffs, P., *Z. physiol. Chem.*, **181**, 83 (1929).

¹²⁶ Discherl, W., *Z. physiol. Chem.*, **219**, 177 (1933); *Brit. Chem. Abs.*, 1933A, 1037.

¹²⁷ Meyer, K., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 341 (1935); *Chem. Abs.*, **30**, 7457 (1936).

¹²⁸ Lipmann, F., *Skand. Arch. Physiol.*, **76**, 186 (1937); *Chem. Abs.*, **31**, 4904 (1937).

¹²⁹ Baur, E., *Helv. Chim. Acta*, **19**, 234 (1936).

¹³⁰ Neiger, R., and Neuschul, P., *Z. physik. Chem.*, **A177**, 355 (1936).

¹³¹ Jaeger, F. M., and Berger, G., *Rec. trav. chim.*, **41**, 71 (1922).

¹³² Euler, H., *Ber.*, **49**, 1366 (1916).

¹³³ Rudberg, E. G., *Z. Physik*, **24**, 247 (1924).

¹³⁴ Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

pendent of the pH of the solution for wave-lengths less than 2300A. Dain and Puzenkin¹³⁵ employ the reaction for absolute actinometric measurements.

The photochemical reactions between the halo-acetic acids and alcohol were studied by Cassel,¹³⁶ who observed decomposition into the unsubstituted acid, acetic aldehyde and the halogen acid. Wave-lengths shorter than 2500A were required. The halogen could be more readily liberated by light from 1-bromosuccinic acid than from 1-chlorosuccinic acid.

A uranyl-sensitized photooxidation of monochloroacetic acid by potassium permanganate has been found of zero order with respect to the oxidant by Ghosh and Ray,¹³⁷ who employed the wave-lengths 3660 and 4360A. Its rate varies as the intensity of the incident radiation and is influenced by the sensitizer concentration.

Trichloroacetic acid decomposes into carbon dioxide and chloroform, the temperature coefficient being 3.6 in light and 4.28 in darkness, according to Banerji and Dhar.¹³⁸ The quantum yields are abnormally high and increase with the temperature and the frequency of the incident radiation.¹³⁹ Solutions in water show some absorption of visible light which is without much photochemical effect, although water acts as photosensitizer. Absorption begins to increase at 3200A, is complete at 3000A, and decreases at shorter wave-lengths.

UNSATURATED ACIDS

The stereoisomeric transformations of unsaturated dicarboxylic acids, direct and sensitized, have been much studied. Kailan¹⁴⁰ found that solid fumaric acid was not converted into maleic acid by ultraviolet light, and that maleic acid could be converted into fumaric only to the very slightest extent. But in aqueous solutions (about 0.084 normal), an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the side of maleic acid with increasing concentrations. At 45° to 50°C., with 0.1N solution the equilibrium mixture contained 75 per cent of maleic acid and in 0.4N solution 79 per cent. The velocity of transformation was much greater in quartz than in glass vessels, but the equilibrium composition was the same.

Earlier observations were recorded by Stoermer with Frederici, Brautigam and Neckel,¹⁴¹ who found that although fumaric acid when irradiated yielded about 70 per cent of maleic acid, sodium fumarate could not be converted into sodium maleate in this manner. The transformation of fumaric acid into maleic acid could also be effected in benzene solution.¹⁴² Stoermer, who has made extensive investigations of the stereoisomeric transformations of ethenoid linkages in a wide variety of compounds, showed that at photochemical equilibrium, the less stable form was present in the larger amount, proving that light does not act merely as a catalyst in hastening a thermal equilibrium.

¹³⁵ Dain, B. Y., and Puzenkin, E. S., *Ber. ukrain. wiss. Forsch.-Inst. physik. Chem.*, **4**, 75 (1934); *Chem. Abs.*, **29**, 2451 (1935).

¹³⁶ Cassel, H. W., *Z. physik. Chem.*, **92**, 113 (1916).

¹³⁷ Ghosh, J. C., and Ray, B. B., *J. Indian Chem. Soc.*, **13**, 1 (1936); *Chem. Abs.*, **30**, 4093 (1936).

¹³⁸ Banerji, S. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **134**, 172 (1924); *Chem. Abs.*, **18**, 2634 (1924).

¹³⁹ Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **209**, 123 (1932); *Chem. Abs.*, **27**, 907 (1933).

¹⁴⁰ Kailan, A., *Z. physik. Chem.*, **87**, 333 (1914); *J. Chem. Soc.*, **106** (ii), 449 (1914); *Monatsh.*, **41**, 305 (1920); *Chem. Abs.*, **15**, 1100 (1921).

¹⁴¹ Stoermer, R., with Frederici, Brautigam, and Neckel, *Ber.*, **44**, 637 (1911).

¹⁴² Stoermer, R., *Ber.*, **42**, 4865 (1909); *J. Chem. Soc.*, **98** (ii), 114 (1910).

Warburg¹⁴⁸ measured the quantum yields for the transformation of each stereoisomer at the wave-lengths 2070, 2530 and 2820Å. The yields were but little affected by the change in wave-length, being slightly greater at 2530Å than at either of the other two. For the conversion of maleic into fumaric acid, the values ranged from 0.032 to 0.049, being slightly greater at lower (0.00514) than at higher (0.0102) concentrations. For the reverse transformation of fumaric into maleic acid, the yields were about twice as great, varying from 0.08 to 0.133. In this case, the higher values were obtained in the more concentrated solutions. The low quantum yields were assumed to be due to the fact that after the initial excitation of the molecule, it tends on collision to return to the original form more frequently than it does to yield the isomer. At 3130Å, Vaidya¹⁴⁴ found the quantum yields for maleic acid to be at 0.01 molar, 0.048, at 0.005 molar, 0.052 and for fumaric acid, 0.117 and 0.083, respectively.

Absorption data for maleic and fumaric acids, their *l*-menthyl and dimethyl esters and maleic anhydride in various solvents were given by Wassermann and Smakula¹⁴⁵ over the range 3000 to 1900Å. Their data were thought not to eliminate the Anschütz cyclic formula for maleic acid.

It has been suggested that maleic and fumaric acids may have a common excited electronic state.¹⁴⁶ Olson¹⁴⁷ has given a theoretical treatment of the conversion. The potential energy wells corresponding to the separate acids are separated by a potential barrier, so that the transformation cannot occur thermally at ordinary temperatures. Olson plotted curves of the potential energy against the angle through which one half of the molecule is twisted relative to the other about the double bond as axis. Such curves for the excited state make evident the manner in which the stabilizing effect of the double bond disappears on excitation of one of the electrons of the bond. From these curves Olson determined by the methods of wave mechanics, the probabilities that on the return of the molecule from the excited state, the *cis* or the *trans* form would result. With Hudson, Olson¹⁴⁸ further developed methods for predicting from the extinction coefficients of the acids at various concentrations and wave-lengths, the compositions of the photo-stationary states when the acids, in several concentrations, are irradiated with various monochromatic wave-lengths. From thermal data, calculations of the heats of isomerization were also made.

Comparison of the absorption spectra of the *cis* and *trans* forms of a number of related stereoisomeric compounds usually show that of the more stable *trans* form to lie closer to the visible. Contrary to this general rule, in the three pairs of compounds, diethyl $\alpha\alpha'$ -diphenylfumarate and maleate, dimethyl $\alpha\alpha'$ -di-*m*-tolylfumarate and maleate, and dimethyl $\alpha\alpha'$ -di-*p*-tolylfumarate and maleate, the absorption curve of the *cis* form is the closer to the visible, and is, therefore, the more stable form at low temperatures. Ramart-Lucas and Hoch¹⁴⁹ prepared these three fumarates by the irreversible action of ultraviolet on the corresponding maleates; this reaction gave, in addition, carbalkoxyarylidones, also formed by the action of ultraviolet light on the dialkyl $\alpha\alpha'$ -diarylfumarates. Irradiation of the

¹⁴⁸ Warburg, E., *Sitzb. Preuss. Akad. Math.-Phys.*, 960 (1919); *Chem. Abs.*, 14, 1931 (1920).

¹⁴⁴ Vaidya, B. K., *Proc. Roy. Soc.*, A129, 299 (1930).

¹⁴⁵ Wassermann, A., and Smakula, A., *Z. physik. Chem.*, A155, 366 (1931).

¹⁴⁶ Bonhoeffer, K. F., and Harteck, P., "Grundlagen der Photochemie," Dresden, Steinkopff, 270, 1933.

¹⁴⁷ Olson, A. R., *Trans. Faraday Soc.*, 27, 69 (1931).

¹⁴⁸ Olson, A. R., and Hudson, F. L., *J. Am. Chem. Soc.*, 55, 1413 (1933).

¹⁴⁹ Ramart-Lucas, Mme., and Hoch, J., *Compt. rend.*, 189, 696 (1929).

sodium salts of the $\alpha\alpha'$ -diarylmaleic acids with ultraviolet light gave the sodium salts of the arylindonecarboxylic acid.¹⁵⁰

The possibility of the photodissociation of the unsaturated acids into carbon dioxide and acids of the acrylic series has been discussed. Volmar¹⁵¹ found that unsaturated dibasic acids undergo photolysis more rapidly than their saturated analogs. That of the *cis* compounds was five to six times as rapid as that of the *trans* forms, the latter behaving like monobasic acids. In the *cis* acids, the carboxyl groups were thought to exert a mutually enhancing effect. Itaconic acid behaved like succinic acid. On prolonged exposure to ultraviolet light, both the *cis* and *trans* forms behave alike after an equilibrium state has been set up. Olson and Hudson found that such photolyses occur with insufficient speed to interfere with their determinations of the stationary states resulting from stereoisomeric transformations.

Berezovskaya, Kogon and Moskalenskaya¹⁵² found that light alone induced only the stereoisomeric changes in maleic and fumaric acids, but that the combined action of ultraviolet light and platinum led to decomposition. The barium salt of fumaric acid reacted similarly to the free acid, but the barium salt of maleic acid underwent no decomposition under these conditions.

The sensitization of the maleic-fumaric conversion to visible light by bromine, described by Wislicenus in 1895, has been extensively studied by Eggert and co-workers.¹⁵³ The ethyl esters were studied in carbon tetrachloride solution. The rate was proportional to the number of quanta absorbed, independent of the bromine concentration within the limits of 1:9, and independent of the carbon tetrachloride concentration within the limits 1:5. At 21°C., with the bromine concentration 0.1*N*, at the wave-length 4360A the quantum yield for the transformation was high, 295. At the same time, some of the bromine was photochemically added to the ester, the quantum yield for this reaction being 8.2.¹⁵⁴ These yields were independent of the intensity of the light and the concentration of the ester from pure ester to 70 moles of solvent per mole of ester. They were also independent of the bromine concentration from 0.03 to 0.3*N*. The intermediary formation of diethyl dibromosuccinate was postulated but no attempt was made to isolate it. Subsequent determinations by Wachholtz¹⁵⁵ at this wave-length showed, at various bromine concentrations, a range of from 108 to a maximum of 755 for the quantum yield for the transformation to fumarate. At 5570A the range was 77 to 307. The temperature and the wave-length employed were the chief determining factors. At the shorter wave-length (4360A) the yield increased approximately from 100 at 0° to 700 at 23°C.; at 5570A from 100 at 16° to 300 at 23°C. Similarly, the yields for the addition reaction depended only upon the temperature, wave-length and bromine concentration, values within the range of 3 to 42 being obtained. Bromine atoms, produced by photodissociation, form a complex short-lived intermediary product. This is considered a radical, since only one bromine atom is present. In a subsequent collision, the bromine atom is again liberated and fumarate formed. The liberation of the bromine permits it to act upon another maleate molecule and so accounts for the very high quantum

¹⁵⁰ See also Biquard, D., *Ann. Chim.*, **20**, 97 (1933), for the change of methyl diphenylmaleate to the fumarate on irradiation of its alcoholic solution, catalyzed by a trace of bromine.

¹⁵¹ Volmar, *Compt. rend.*, **181**, 467 (1925).

¹⁵² Berezovskaya, F. I., Kogon, M., and Moskalenskaya, E., *Compt. rend. acad. sci. U.R.S.S.*, **4**, 50 (1934); *Chem. Abs.*, **29**, 2089 (1935).

¹⁵³ Eggert, J., *Physik. Z.*, **24**, 504 (1923); *Chem. Abs.*, **18**, 3548 (1924).

¹⁵⁴ Eggert, J., Wachholtz, F., and Schmidt, R., *Physik. Z.*, **26**, 865 (1925).

¹⁵⁵ Wachholtz, F., *Z. physik. Chem.*, **125**, 1 (1927).

yields. In the event of a collision of the radical with a bromine molecule, it is possible that dibromosuccinic ester may be formed with liberation of a bromine atom.

In the case of the methyl ester (and also of the free acids), the quantum yields of the transformation and addition reactions are independent of the variation of the ester concentration and of the radiation intensity at high concentrations. At low concentrations, however, the yield for the isomerization decreases with decreasing ester concentration and with increasing intensity. Both this and the yield of the addition reaction are markedly dependent upon the temperature, as in the case of the ethyl ester.¹⁵⁶ The yield for the addition reaction depended upon the bromine concentration. The effect of change of wave-length (4360Å, 5470Å) is as follows: ethyl ester, ratio of yields at 4360 to 5470Å, 1.9, methyl ester, 2.3. For the addition reaction, the corresponding values were 2.3 and 1.9. For free maleic acid, the ratio of the yields for the isomerization were 5·4·1, for ultraviolet, blue and green light.

In the system: maleic acid, sulfuric acid and bromine, at high concentrations of maleic acid, the transformation quantum yield is 430 at 21°C.¹⁵⁷ At lower concentrations of maleic acid, it is less, and becomes dependent on both the light intensity and the concentration of the maleic acid. The light reaction may, under these conditions, be initiated by the reduction of bromic acid, hypobromous acid and bromine. Reduction of bromine by ferrous sulfate gives a yield of 10,000 molecules of fumaric acid per atom of bromine formed. The yield is practically independent of the concentration of the reactants as long as the ferrous ion concentration is less than 10^{-5} , but at higher concentrations it becomes dependent on the ferrous ion concentration. These studies were undertaken to provide additional evidence that bromine atoms are responsible for the photosensitized conversion.¹⁵⁸

The quantum yield of the addition of bromine to dimethyl fumarate is of the order of magnitude found by Wachholtz for the bromination of diethyl maleate or fumarate. It is not essentially different when aqueous solutions are used.

Mercuric bromide and mercurous nitrate and perchlorate are said also to sensitize the photochemical change of maleic to fumaric esters.

Stoermer and Robert¹⁵⁹ found the rearrangement of the amide of crotonic acid into that of isocrotonic acid to be easily effected by a Uviol lamp. By the aid of a Heraeus quartz lamp, they effected to some extent the conversion of the corresponding acid. Under the influence of ultraviolet light, it was also easily possible to secure the addition of the elements of water, methyl or ethyl alcohol to the double bond. Aniline and ammonia also add with the greatest ease at the double bond of α,β -unsaturated acids; crotonic acid and aniline give, together with a little of the anilides of crotonic and isocrotonic acids, chiefly $\text{CH}_3\text{CH}(\text{NHC}_6\text{H}_5)\text{CH}_2\text{COOH}$ and some of its anilide, while ammonia yields chiefly $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{COOH}$ and iminodibutyric acid, with only very little of the amide of crotonic acid.

The separation of the two anilides is extraordinarily difficult and even on irradiating the pure stable anilide the amount of isoanilide obtained was not sufficient to permit of complete separation by careful fractional crystallization.

¹⁵⁶ Eggert, J., Wachholtz, F., and Schmidt, R., *Z. Elektrochem.*, **33**, 542 (1927).

¹⁵⁷ Wachholtz, F., *Z. Elektrochem.*, **33**, 542, 545 (1927).

¹⁵⁸ See also *Oesterr. Chem. Ztg.*, **30**, 110 (1927); *Z. physik. Chem.*, **135**, 147 (1928); Schmidt, R., *Z. physik. Chem.*, **B1**, 205 (1928).

¹⁵⁹ Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922); *Chem. Abs.*, **8**, 2880 (1914); **16**, 3631 (1922).

With the Heraeus lamp the maximum rearrangement (40 per cent) of the amide of crotonic acid in acetone is attained in about two days. For the rearrangement of crotonic acid, toluene proved the best solvent.

Acrylic acid similarly treated with aniline gives $C_6H_5NHCH_2CH_2CONHC_6H_5$ and the deliquescent hydrochloride, melting about $64^\circ C.$, of $C_6H_5NHCH_2CH_2COOC_2H_5$, a light yellow oil. From crotonic acid and paratoluidine was obtained ethyl β -*p*-toluidineobutyrate.

The conversion of the α -methylated mesaconic acid into citraconic acid is very difficult. In solution in water or methyl alcohol, the solvent appears to combine with the acid.¹⁶⁰ Quantum yields of 0.18 at 0.01 molar and 0.22 at 0.005 molar were reported by Vaidya¹⁶¹ for 3130A for the isomerization of citraconic acid.

The acrylic acid esters prepared from glycerine, lactic acid, etc. when exposed to sunlight or ultraviolet light polymerize to varnish-like elastic masses. They are soluble in solvents for oils and are said to dry rapidly and not to be readily affected by exposure or by chemical agents.¹⁶²

Malachowski and Maslowski¹⁶³ have prepared the α -, β -, and γ -*trans*-monomethyl esters of aconitic acid by irradiating the *cis* compounds in the presence of bromine by direct sunlight or a mercury arc.

Little, if any, work has been done on the photochemistry of the higher saturated fatty acids, but the long-chained unsaturated fatty acids have been frequently studied. The results of this work are discussed in Chapter 30 in connection with the behavior of drying oils.

COMPOUNDS CONTAINING NITROGEN

Cyanogen Compounds. Hydrogen cyanide has no absorption spectrum between 2800A and 2100A but possesses a series of bands between 2001 and 1789A.¹⁶⁴ A few observations on the decomposition of hydrogen cyanide in cherry-laurel water have been reported by Andant and Rousseau.¹⁶⁵ They believed, since they found about as much (slight) decomposition to be effected by the 3650A line as by the total radiation of an arc to 3130A, that ultraviolet effects are nullified by the longer wave-lengths. They state that 0.126 gm. of manganese chloride in cherry-laurel water increases the action of ultraviolet rays so that the loss of hydrocyanic acid reaches 10.1 per cent in the first thirty minutes of irradiation and 30.0 per cent after two hours. They were inclined to attribute the activity to visible light.

Cyanogen is transformed into paracyanogen by ultraviolet rays.¹⁶⁶ On exposure to sunlight, cyanogen slowly polymerizes. In the presence of oxygen and ultraviolet light, it is oxidized completely to carbon dioxide and nitrogen. Hogness and Tsai,¹⁶⁷ observed in cyanogen gas at one atmosphere a series of diffuse bands beginning at 2240A and extending to the limits of dispersion of the quartz of their

¹⁶⁰ Stoermer, R., *Ber.*, 44, 637 (1911).

¹⁶¹ Vaidya, B. K., *Proc. Roy. Soc.*, A129, 299 (1930).

¹⁶² Morrell, R. S., and de Waele, A., "Rubber, Resins, Paints and Varnishes," New York, D. Van Nostrand Company, Inc., 1921.

¹⁶³ Malachowski, R., and Maslowski, M., *Ber.*, 61B, 2521 (1928).

¹⁶⁴ Villars, D. S., *J. Am. Chem. Soc.*, 52, 61 (1930); Hilgendorf, H. J., *Z. Physik*, 95, 781 (1935).

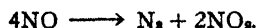
¹⁶⁵ Andant, A., and Rousseau, E., *Compt. rend.*, 184, 683, 1553 (1927); *Compt. rend. soc. biol.*, 96, 613 (1927); *Chem. Abs.*, 21, 3161 (1927).

¹⁶⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, 150, 1169 (1910); *J. Chem. Soc.*, 98, ii, 349 (1910).

¹⁶⁷ Hogness, T. R., and Tsai, L. S., *J. Am. Chem. Soc.*, 54, 123 (1932).

spectrograph. Their diffuse nature indicated the primary process to be one of predissociation, the available evidence indicating the products to be two CN molecules, one of which is excited.¹⁶⁸ The quantum efficiency for the polymerization by a hydrogen discharge source was found to be three. These authors were unable to confirm the observations of Berthelot and Gaudechon with the mercury arc, since cyanogen does not absorb any mercury lines.

Norrish and Smith¹⁶⁹ have described two reactions occurring when a mixture of nitric oxide and cyanogen is illuminated by radiations between 3600 and 2200Å.

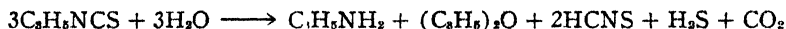


In the first of these, which occurs six times as extensively as the second, the cyanogen plays the part of a catalyst. Neither reaction occurs in the absence of a small amount of oxygen, which accumulates as the reaction proceeds, the effect being autocatalytic. The previously unknown molecule, NOCN, was suggested as an intermediary product.

A carbon tetrachloride solution of thiocyanogen $(\text{SCN})_2$, according to Kaufmann and Liepe,¹⁷⁰ polymerizes readily in the sunlight. In ethereal solutions, substances having powerful odors are formed. Soderbäck¹⁷¹ finds the addition of thiocyanogen to ethylenic hydrocarbons, which is very slow at ordinary temperatures, to go smoothly when the reactants are exposed in dry benzene solution to the action of actinic rays, yielding dithiocanoethanes of the type CNS.CHR. CHR.CNS. Only two thiocyanogen radicals will combine with acetylenic hydrocarbons, giving compounds of the type $\text{CR}'(\text{CNS})=\text{CR}'\text{CNS}$. Aromatic acetylene derivatives combine readily at the ordinary temperature in the dark, but aliphatic acetylenes require intense photocatalysis to cause addition. Interconversion of *cis* and *trans* forms under the influence of ultraviolet light occurs with the compounds obtained from acetylenes, a 0.02*N* solution of free thiocyanogen in benzene being an effective catalyst for the change. Acetylene itself yields a solid *s*-dithiocanoethylene, melting 97-98.5°, and a liquid form, melting 15-17°, which are interconvertible under the influence of light.

Irradiation of fumaronitrile in acetone with ultraviolet light for 100 hours gives maleonitrile and an additive compound.¹⁷²

Ganassini¹⁷³ finds that sunlight produces a yellow color in allylisothiocyanate and that, after a month, it deposits a precipitate. In the presence of water, decomposition occurs to the extent of 5 per cent and, in its absence, to the extent of 15 per cent, air being present in either case. He suggested the following possible reactions.



Sulfuric acid and ammonia are also formed by secondary reactions.

The polymerization of methylacrylonitrile in ultraviolet light has been described

¹⁶⁸ See also Mooney, R. B., and Reid, H. G., *Nature*, **128**, 271 (1931).

¹⁶⁹ Norrish, R. G. W., and Smith, F. F. P., *Trans. Faraday Soc.*, **24**, 620 (1928)

¹⁷⁰ Kaufmann, H. P., and Liepe, J., *Ber.*, **56B**, 2514 (1923)

¹⁷¹ Söderbäck, E., *Annalen*, **443**, 142 (1925).

¹⁷² Jennen, J., *Bull. soc. chim. Belg.*, **46**, 258 (1937); *Brit. Chem. Abs.*, **A** 11, 404 (1937), *Chem. Abs.*, **32**, 500 (1932).

¹⁷³ Ganassini, D., *Arch. ist. biochim. ital.*, **3**, 1 (1931); *Chem. Abs.*, **26**, 2657 (1932).

by Mertens and Fonteyn.¹⁷⁴ Considerable information has been obtained regarding the absorption spectra of the nitriles and amides of many acids.¹⁷⁵

Amines. Dissolved in hexane, ammonia has a band at about 1920A, which is displaced toward shorter wave-lengths in aqueous solution.¹⁷⁶ Other amines exhibit similar solvent effects.

In the gaseous state, the amines exhibit a series of diffuse predissociation absorption bands, increasing in intensity toward the shorter wave-lengths, and attributed to an electronic excitation in the amino- group.¹⁷⁷ In methylamine the predissociation bands begin at 2440A and in ethylamine at 2370A.¹⁷⁸

Berthelot and Gaudechon¹⁷⁹ found ethyl- and methylamine, guanidine, and hydroxylamine, when subjected to ultraviolet radiations, to be converted first into ammonia and then into nitrites. Emeléus and Jolley state that methylamine, on exposure to light from a mercury arc or an aluminum spark, produces equal amounts of ammonia and hydrogen and a liquid, with small quantities of methane and nitrogen. Ethylamine gives the same gaseous products and small quantities of ethane and ethylene. Benzene has also been found among the products.¹⁸⁰ Decomposition quantum yields of about 0.75 are found. The primary reaction is believed to form CH_3NH and H , rather than CH_3 and NH_2 .¹⁸¹ The photo-oxidation of methylamine yields principally ammonia; the quantum yield is again 0.75.

In the presence of zinc oxide, or titanium dioxide, the aliphatic amines are oxidized to nitrites in sunlight more readily than are the aromatic amino- derivatives. The amines are first hydrolyzed and then the ammonia is oxidized to nitrite and the alcohol to an aldehyde.¹⁸²

Amides. Berthelot and Gaudechon¹⁸³ state that equal volumes of carbon monoxide and ammonia combine in a few hours to give formamide under the influence of rays of wave-length about 2000A to 3000A. Formamide also slowly decomposes when submitted to ultraviolet rays, the reaction being complicated by dehydration and formation of hydrogen cyanide. Light, less markedly than heat, produces polymerization.¹⁸⁴ The titanium dioxide-sensitized decomposition in sunlight proceeds more rapidly in the amides of monobasic than in those of dibasic acids.¹⁸⁵

On exposure to ultraviolet rays¹⁸⁶ urea is said to be converted first into ammonia and then into a nitrite. Kailan,¹⁸⁷ however, found that a normal solution

¹⁷⁴ Mertens, E., and Fonteyn, M., *Bull. soc. chim. Belg.*, **45**, 438 (1936); *Chem. Abs.*, **30**, 8152 (1936).

¹⁷⁵ Bruylants, P., and Castille, A., *Bull. soc. chim. Belg.*, **34**, 261 (1925); Castille, A., and Gueudens, J., *Ann. soc. scient. Bruxelles*, **47B**, 56 (1927); Castille, A., and Ruppel, E., *Bull. sci. acad. roy. Belg.*, **16**, 1129 (1930); *Bull. soc. chim. Belg.*, **40**, 243 (1931); **44**, 351 (1935); Castille, A., *Bull. sci. acad. roy. Belg.*, **16**, 811 (1930); Ruppel, E., *Bull. sci. acad. roy. Belg.*, **21**, 236 (1935); Herzberg, G., and Scheibe, G., *Trans. Faraday Soc.*, **25**, 716 (1929).

¹⁷⁶ Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); for the absorption of alkyl amines, see Ramart-Lucas, Mme., *Compt. rend.*, **194**, 726 (1932); Grunfeld, M., *Ibid.*, **194**, 1083 (1932).

¹⁷⁷ Herzberg, G., and Kölsch, R., *Z. Elektrochem.*, **39**, 572 (1933). Analyses of the methylamine bands have been given by Henri, V., and Lasareff, W., *Compt. rend.*, **200**, 829 (1935); *J. chim. phys.*, **32**, 353 (1935).

¹⁷⁸ Emeléus, H. J., and Jolley, L. J., *J. Chem. Soc.*, 1612 (1935).

¹⁷⁹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

¹⁸⁰ Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 2370 (1931).

¹⁸¹ Emeléus, H. J., and Jolley, L. J., *loc. cit.*

¹⁸² Rao, G. G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Brit. Chem. Abs.*, **A** 1316 (1934).

¹⁸³ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 207 (1912).

¹⁸⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1164 (1910); **151**, 478 (1910).

¹⁸⁵ Rao, G. G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Chem. Abs.*, **29**, 1326 (1935).

¹⁸⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

¹⁸⁷ Kailan, A., *Z. physik. Chem.*, **95**, 215 (1920); *J. Chem. Soc.*, **118** (ii), 576 (1920).

of urea irradiated for 48 hours by a quartz mercury lamp (or for 1632 hours with the rays from 80 mg. of radium) showed no change in density, refractive index, or rate of change into ammonium cyanate, other than could be accounted for by experimental error.

Azomethane. This compound begins to absorb at about 4000Å, exhibits a maximum at 3390Å, a minimum at 2700Å and increasing absorption at shorter wave-lengths. No evidence of definite bands appears.¹⁸⁸

Ramsperger followed the photodecomposition by pressure measurements from which he concluded the reaction to be mainly



He found the temperature coefficient to be about zero and the quantum yield two, the latter remaining practically constant over a two hundred-fold pressure range. To explain this result, Ramsperger made the assumption that the ethane molecule bore enough energy, derived from the heat of reaction and from the excess energy of the 3660Å line employed over the energy required for the photodecomposition, to effect the decomposition of a second molecule of azomethane on collision with it. This theory would, however, be difficult to reconcile with the independence of the quantum yield and the pressure.

Since Ramsperger had used the "treacherous method of filters" in his quantum yield determinations, Forbes, Heidt and Sickman¹⁸⁹ repeated them, using for the energy determinations the uranyl oxalate actinometer. They made determinations at six wave-lengths of monochromatic light and at various pressures. At low pressures they found the quantum yield to approach unity as its upper limit, at least for the initial decomposition. It decreases with increasing decomposition at room temperature and also with increasing pressures. The latter points to a collisional deactivation. It was necessary in the measurements to use a graphical method of correcting for errors due to the deposition of difficultly volatile decomposition products upon the window. The quantum yields passed through a maximum in the region 3660 to 3350Å, corresponding to the maximum of absorption by the N—N bond. At shorter wave-lengths they decreased, but began to increase again when wave-lengths absorbed by the N—C bond were employed. In agreement with Ramsperger, the temperature coefficient was zero at temperatures below 260°C.

That the decomposition is not a chain reaction between 20° and 226°C. was confirmed by Patat,¹⁹⁰ who believed the primary reaction to yield nitrogen and two methyl groups. His evidence for this was the fact that dimethyl ether at 150 to 600 mm. pressure could be decomposed in the presence of 10 to 30 mm. of irradiated azomethane. That the free methyl radicals did not form chains indicated the activation energy for the reaction between methyl and azomethane to be greater than 20 kcal. Burton, Davis and Taylor¹⁹¹ believe quantum yield determinations based only on the pressure increase are too low. They find the amount of nitrogen produced in experiments at various temperatures always exceeds that of the hydrocarbons. The excess is a maximum at about 200°C. Methane increases and ethane decreases at the higher temperatures. The amount of higher

¹⁸⁸ Ramsperger, H. C., *J. Am. Chem. Soc.*, **50**, 123 (1928); for observations on azoisopropane, see *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

¹⁸⁹ Forbes, G. S., Heidt, L. J., and Sickman, D. V., *J. Am. Chem. Soc.*, **57**, 1935 (1935); see also Heidt, L. J., and Forbes, G. S., *Ibid.*, 2331.

¹⁹⁰ Patat, F., *Naturwiss.*, **23**, 801 (1935); *Nachr. ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe II*, [N.F.], **2**, 77 (1936); *Chem. Abs.*, **31**, 6112 (1937).

¹⁹¹ Burton, M., Davis, T. W., and Taylor, H. A., *J. Am. Chem. Soc.*, **59**, 1038, 1989 (1937).

hydrocarbons increases with the degree of decomposition and with lowering of temperature. No hydrogen and only a little unsaturated hydrocarbon are produced. Burton, Davis and Taylor doubt that the temperature coefficient is zero below 226°C. They suggest the occurrence of a secondary association reaction between methyl radicals and $(\text{CH}_3\text{N})_2$. When nitric oxide is present during photolysis, practically no alkane gas is produced.¹⁹² From analyses of the reaction under these conditions, it is concluded that the source of ethane and other alkanes in the ordinary photolysis is not the combination of free radicals, but the decomposition of the association product with azomethane.

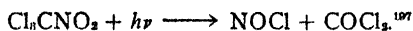
Diazo-Compounds. Diazomethane exhibits an absorption spectrum somewhat resembling that of azomethane.¹⁹³ It consists of a series of weak diffuse bands in the region 4710 to 4250Å, followed by a continuum from 4250 to 3200Å, and a second completely continuous region beginning at 2650Å. The photochemical decomposition is unimolecular; the main products are nitrogen, ethylene, ethane and a non-volatile liquid. The quantum yield is approximately four at 3650 and 4360Å. The primary process is the decomposition: $\text{CH}_2\text{N}_2 + h\nu \rightarrow \text{CH}_2 + \text{N}_2$. This is supported by the behavior of mixtures of the gas with hydrogen and with oxygen.

Adamson and Kenner¹⁹⁴ find that vinyl diazomethane, $\text{CH}_2=\text{CHCH}=\text{N}_2$, in 0.5-per cent ether solution forms pyrazole by a monomolecular photochemical reaction.

Ethyl diazoacetate, as such or in various solvents,¹⁹⁵ has an absorption curve similar to that of compounds containing a carbonyl group since both chromophores $\text{N}=\text{N}$ and CO are said to have the same electron-term scheme. In the photolysis in heptane solution, the quantum yield rises from 0.20 for 4200Å to 1.11 for 2600Å; the rate of increase is small at first, but becomes greater in the band of shorter wave-length. In ethanol, methanol and water, there is a similar rise, but compared with heptane the values are smaller in the longer ultraviolet and greater in the shorter. For a given wave-length, the quantum yield either rises or falls in the order: heptane, ethanol, methanol, water. Neither a ten-fold increase in concentration nor a rise in temperature from 5° to 40°C. affects the quantum yield.

Goldfinger¹⁹⁶ measured manometrically photodecomposition by the full radiation of the mercury arc at various initial pressures from 0.04 to 297 mm. The relative velocity is greatest for the lowest pressure; the order of the reaction lies between zero and two. At low pressures, it is accelerated by argon. At higher pressures, it is retarded by nitrogen and by methane.

Nitro-Compounds. Chloropicrin is decomposed by violet or ultraviolet light, but the reaction soon stops because the nitrosyl chloride formed acts as an internal filter.



According to Thompson and Purkis¹⁹⁸ methyl nitrite yields on photolysis a solid containing paraformaldehyde and formic acid, with small amounts of carbon

¹⁹² Davis, T. W., Jahn, F. P., and Burton, M., *J. Am. Chem. Soc.*, **60**, 10 (1938).

¹⁹³ Kirkbride, F. W., and Norrish, R. G. W., *J. Chem. Soc.*, 119 (1933).

¹⁹⁴ Adamson, D. W., and Kenner, J., *J. Chem. Soc.*, 286 (1935).

¹⁹⁵ Wolf, E., *Z. physik. Chem.*, **B17**, 46 (1932).

¹⁹⁶ Goldfinger, G., *Compt. rend.*, **202**, 1502 (1936).

¹⁹⁷ Radulescu, D., and Zamfirescu, G., *Bul. soc. chim. Romania*, **17**, 87 (1935); *Chem. Abs.*, **30**, 671; see also Piutti, A., *Atti I Congr. naz. Chim. pura applicata*, 437 (1923); *J. Chem. Soc.*, **120**, 298 (1921); Piutti, A., and Mazza, F. F., *Gas. chim. ital.*, **57**, 610 (1927); Alekseevskii, E. V., *J. gen. Chem. (U.S.S.R.)*, **2**, 341 (1932).

monoxide and hydrogen, and 45 per cent each of nitrogen and nitrous oxide. In the case of ethyl nitrite, the volume decrease is less and the fraction of non-condensable gases is larger. Aldehydes are present in a liquid residue. The residual gas has 38 per cent of nitrogen, 30 per cent of nitrous oxide, 18 per cent of carbon monoxide and 13 per cent of methane.

In the wave-length range 2000 to 3000Å, the primary process is believed¹⁹⁹ to be in the case of nitro-compounds



This is followed by certain reactions of NOH and by oxidation of the aldehyde.

It is assumed that light absorbed by the molecule $\text{R}-\text{CH}_2-\text{N} \begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$ changes it to

the form $\text{RCH}=\text{N} \begin{smallmatrix} \text{OH} \\ / \\ \text{O} \end{smallmatrix}$, and that this is followed by a rupture of the molecule.

In the photolysis of tetramethylene nitrosochloride, the primary process, according to Hammick and Lister²⁰⁰ is the elimination of NOH, the resulting olefin undergoing further reactions. The quantum yield is approximately unity. If the carbon atom to which the NO group is attached is also linked to an atom other than carbon, a photooxidation occurs in the presence of oxygen with unit quantum efficiency. In the absence of oxygen, 1-chloro-1-nitroso-cyclohexane undergoes a rapid photoreaction without the evolution of gas. Red light decomposes nitroso-isopropylacetone to $\text{H}_2\text{N}_2\text{O}_2$ and its decomposition products and mesityl oxide. β -nitroso- β,ϵ -dimethylhexane probably gives a β,ϵ -dimethylhexene.²⁰¹

Milone²⁰² finds ultraviolet irradiation to isomerize the α - and γ -forms of certain glyoximes, both in the solid state and in dilute alcohol, at 18°C., to the β -forms. The isomerization is also promoted very slowly by sunlight, but Wood light (3650Å) is ineffective. Isomerization is more rapid in 30-40-per cent ethyl alcohol than in the solid state, as shown by the following data, which give the hours of exposure and the percentage of β -compound formed in solution and in the solid state, respectively: α -phenylglyoxime, 23,44.8; 17,20.7; α -*p*-tolylglyoxime, 22,28.8; 19,20.2; α -methylphenylglyoxime, 21,30.3; 19,15; α -diphenylglyoxime, 26,29; 20,15.9; γ -diphenylglyoxime, 28,41; 19,22.4. In sunlight, behind glass, γ -phenylglyoxime yielded only 0.93 per cent of the β -compound after 16 months.

After thirty minutes of exposure to ultraviolet rays, 0.10 gm. of nitroglycerin at 20 mm. gave 1.32 cc. of gas containing carbon dioxide, 24 per cent, carbon monoxide, 10.5 per cent, nitrogen, 17.5 per cent, nitrous oxide, 8.5 per cent and nitric oxide 39.5 per cent.²⁰³ Some nitric oxide was destroyed in attacking the mercury in the testing apparatus. The high percentage of nitric oxide explains

¹⁹⁹ Thompson, H. W., and Purkis, C. H., *Trans. Faraday Soc.*, **32**, 674, 1466 (1936); for absorption data on nitrites and nitro-compounds, see also Goodeve, C. F., *Trans. Faraday Soc.*, **30**, 504 (1934); Kuhn, W., and Lehmann, H. L., *Z. physik. Chem.*, **18B**, 32 (1932).

²⁰⁰ Hirschlauff, E. N., and Norrish, R. G. W., *J. Chem. Soc.*, 1580 (1936), see also Thompson, H. W., and Dainton, F. S., *Trans. Faraday Soc.*, **33**, 1546 (1937), for the decomposition of alkyl nitrites.

²⁰¹ Hammick, D. L., and Lister, M. W., *J. Chem. Soc.*, 489 (1937).

²⁰² Anderson, K. D., Crumpler, C. J., and Hammick, D. L., *J. Chem. Soc.*, 1679 (1935).

²⁰³ Milone, M., *Gazz. chim. ital.*, **63**, 744 (1933); *Chem. Abs.*, **28**, 2713 (1934).

²⁰⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

its presence in the products of decomposition of smokeless powders containing nitroglycerin.

Berthelot and Gaudechon²⁰⁴ made this behavior the basis of a test for the stability of smokeless explosives. Samples were cut into cylinders weighing 0.25 to 0.45 g., placed over mercury in a quartz tube, containing nitrogen or carbon dioxide, and exposed to the radiations from a quartz mercury lamp at a distance of 78 to 80 mm. for six hours. Powders consisting only of nitrated cellulose were thought to be more stable than those containing nitroglycerin. An English Cordite containing 30 per cent of the latter and 5 per cent of Vaseline, exposed in one cubic centimeter of carbon dioxide, gave a mixture composed of the following volumes of gases: CO₂, 1 cc.; CO, 0.17 cc.; NO, 0.10 cc.; N₂O, 0.02 cc.; N₂, 0.10 cc. Results were also given for the French A and B powders and for Balistite of different ages and with stabilizers.

Experiments were also made in oxidizing (oxygen), reducing (hydrogen) and inert (carbon dioxide, nitrogen) atmospheres.²⁰⁵ With oxygen, two-thirds of the free oxygen disappeared and added its oxidizing effect to that of the oxygen of the nitrocellulose. With hydrogen, about one-quarter disappeared, forming water and formaldehyde. With carbon dioxide, much depended on the temperature. At 25° to 30°C. (70 to 80 mm. from the lamp) there was absorption, due no doubt to the solvents and stabilizers which are basic in their character; at 40°C. (50 mm. distance) no change in volume occurred; at 75°C. (20 mm. distance) there was disengagement of carbon dioxide from the powder and the final volume showed an increase. Nitrogen had no effect on the evolution of nitrogen or nitrous gases from the powder.

Comparison²⁰⁶ of two powders of the same age and make and stabilized by amyl alcohol and diphenylamine, respectively, showed that at 20 mm. (75°C.) amyl alcohol is the more efficient, the latter powder giving off less gas, and the gas containing a very much lower percentage of nitric oxide than the former. At 50 mm. (40°C.), on the other hand, diphenylamine is the more efficient stabilizer. Similar results were obtained with two naval powders, save that these evolved no nitrogen oxides. When the powders were treated with alkali (one gram with 20 cc. of 0.5*N* potassium hydroxide for 30 minutes at 15°C.), it was found that the diphenylamine powder showed less decomposition than that stabilized with amyl alcohol. A damaged naval powder, in which the brownish-yellow plates showed whitish stripes, was examined by the lamp. At both distances, the damaged part gave off more gas than the unaltered part, and this gas contained from 12 to 30 per cent of nitrogen oxide, while the gas from the unaltered part contained none.

A piece of nitrocellulose (collodion) 15 by 51.6 mm., after two hours at 20 mm., gave 0.87 cc. of gas, the percentages of its constituents being CO₂ 25.5, CO 10.5, NO 39, N₂O 7, N₂ 9.²⁰⁷ Collodion, though less heavily nitrated than the French service smokeless powders, decomposed more readily and evolved a notable amount of nitric oxide.

Holmes and Patrick²⁰⁸ stated that celluloid, when exposed to ultraviolet light, becomes brown and brittle with liberation of gaseous products, and that it not only absorbed liquid but the gel itself is decomposed by the rays. More recently,

²⁰⁴ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **153**, 1220 (1911).

²⁰⁵ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 514 (1912).

²⁰⁶ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

²⁰⁷ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

²⁰⁸ Holmes, E. O., Jr., and Patrick, W. A., *J. Phys. Chem.*, **26**, 25 (1922).

however, Clément, Rivière and Beck²⁰⁹ state that ultraviolet light does not exert a destructive effect on celluloids, or nitrocelluloses; instead, it seems to effect a molecular polarization which renders them difficult of esterification. Nitrocellulose, loose or in the form of collodion, decreases considerably in viscosity and the alcohol solubility increases. This is true, however, of only high-viscosity nitrocellulose. Samples with very low viscosities are unaffected by ultraviolet light. Traces of phenolic compounds produce intense yellow coloration with nitrocellulose products exposed to ultraviolet. The viscosity of acetone-soluble nitrocellulose also decreases on exposure but the degree of acetylation is unaffected. Films of cellulose acetate containing phenolic compounds become colored when irradiated. The irradiation of benzyl cellulose, in powder form, results in the formation of a high content of insoluble matter; irradiation of a benzyl cellulose solution does not decrease its viscosity. Other celluloses remain stable when irradiated; the viscosity of ethyl cellulose Celloidin is considerably reduced by irradiation. (See further Chapter 30.)

Long exposure of mercury fulminate, $\text{Hg}(\text{ONC})_2$, to ultraviolet converts it to a black, more flammable but less explosive compound of equal mercury content.²¹⁰

SULFUR COMPOUNDS

Carbon disulfide in admixture with argon undergoes a partial decomposition when exposed to bright sunlight and the sides of the containing vessel become coated with a brown deposit;²¹¹ when exposed to diffused light, it remains unaltered. Bruhat and Pauthenier²¹² have observed the decomposition of carbon disulfide by ultraviolet rays. When this substance is exposed in quartz cells to the quartz mercury arc, a deposit of sulfur is formed on the walls. In order to fix the sulfur, the interior of the cells was coated with a thin film of silver, which is transparent to the ultraviolet. For a six-hour exposure, the long wave-length limit of decomposition was found to be at 3660 Å.

Light catalyzes a reaction of mercaptan in contact with copper and with mercury in the presence of air.²¹³ When aqueous neutral solutions or alkaline solutions of sodium hydrosulphide, ethyl mercaptan, thioglycolic acid, cysteine, etc., are exposed to the radiation of a strong mercury arc, hydrogen is produced with the simultaneous formation of the corresponding disulfide compound. The quantum efficiency with respect to hydrogen formation is always much less than one, indicating that reverse reactions occur. The primary process is probably a decomposition into RS and H. In aqueous solution, where a certain amount of the anion RS' is present the process may be $\text{RS}'(\text{HOH}) + h\nu \rightarrow \text{RS} + \text{H} + \text{OH}'$. This is followed by the formation of hydrogen from hydrogen atoms and of RSSR from two RS. A splitting of the RSII compound into RH and S may also occur as the primary process.

Many sulphydryl compounds react with fluorescent dyestuffs in the dark. Irradiation with light absorbed by the dyestuff accelerates this reaction.²¹⁴

Rathke²¹⁵ showed that the photopolymerization product of thiophosgene is a

²⁰⁹ Clément, L., Rivière, C., and Beck, A., *Chimie et industrie*, Special No. 702 (March, 1932); *Chem. Abs.*, 26, 3662 (1932).

²¹⁰ Patry, M., and Laffitte, P., *Bull. soc. chim.*, 51, 1205 (1932).

²¹¹ Berthelot, D., *Ann. Chim. Phys.*, 19, 150 (1900).

²¹² Bruhat, G., and Pauthenier, M., *Compt. rend.*, 178, 1536 (1924).

²¹³ Dittrich, E., *Brennstoff-Chem.*, 15, 148 (1934); *Chem. Abs.*, 28, 5806 (1934).

²¹⁴ Weiss, J., and Fishgold, H., *Nature*, 137, 71 (1936).

²¹⁵ Rathke, B., *Ber.*, 21, 2539 (1888).

dimer. Schönberg and Stephenson²¹⁶ confirm this, but believe it to be 2,2,4,4-tetrachloro-1,3-dithiacyclobutane, $\text{Cl}_2\text{C} < \begin{smallmatrix} \text{S} \\ \text{C} \end{smallmatrix} > \text{CCl}_2$ rather than $\text{ClCS}_2\text{CCl}_3$, and that its condensation product with aniline is 4,4-dichloro-1,3-dithiacyclobutane-2-one anil. It turns brown when illuminated a short time and is depolymerized to thiophosgene in petroleum ether by the light of a quartz lamp.

Lifschitz and Froentjes²¹⁷ prepare the β -form of ethyl- α -thiolactic acid platinum, $\text{Pt}(\text{CH}_3\text{CHSC}_2\text{H}_5\text{COO})_2$, from the α -form by exposure to the quartz mercury lamp, or better by exposure in aqueous solution to direct sunlight.

ORGANOMETALLIC COMPOUNDS

Lead tetramethyl and tetraphenyl decompose in ultraviolet light, which is absorbed continuously, into metallic lead and hydrocarbons. The former yields methyl radicals. For the vapor phase reaction, the quantum yield is 1.11, but in trimethylpentane, it is about 0.39, as determined by a method employing radioactive indicators. In the vapor phase reaction, oxygen breaks the chains.²¹⁸ The absorption spectrum of dimethyl zinc shows a continuum at approximately 2400Å, that of diethyl zinc shows diffuse bands with an overlapping continuum at approximately 2400Å, and lead tetraethyl shows a quite sharp band in the region between 2300 and 2700Å.²¹⁹

Mercury dimethyl, irradiated by the 2537Å line, yields mercury, methane and ethane with a quantum yield of unity. Ethane constitutes 93 per cent of the hydrocarbons.²²⁰ Methane is formed in amounts increasing at increasing temperatures. The primary process may yield mercury and ethane directly, although subsidiary processes may give free methyl radicals. At 462°K the quantum yield rises to 2.21, chains being involved. At room temperature in the presence of nitric oxide, a white solid is formed, but the quantum yield for the disappearance of mercury dimethyl is still unity. Aerosols²²¹ have been prepared by the photochemical decomposition of mercury dimethyl.

Space does not permit the discussion of the interesting chemiluminescence of the Grignard compounds, nor of their photovoltaic effects.²²²

Little work has been reported on the effects of irradiating such compounds. Gilman and Heck²²³ note that although either heat or ultraviolet irradiation transforms isobutyl bromide to tertiary butyl bromide reversibly, irradiation produces no effect on isobutyl magnesium bromide or tertiary butylmagnesium chloride.

Müller, Frankenburger and Grassner²²⁴ remove metal carbonyls from synthetic methanol or other liquids containing less than 10 per cent of iron or other metal carbonyl by exposure to ultraviolet rays, which also act on any aldehydes or ketones present. According to Reihlen, Gruhl and von Hessling²²⁵ irradiation

²¹⁶ Schönberg, A., and Stephenson, A., *Ber.*, **66B**, 567 (1933).

²¹⁷ Lifschitz, I., and Froentjes, W., *Z. anorg. Chem.*, **224**, 173 (1935).

²¹⁸ Leighton, P. A., and Mortensen, R. A., *J. Am. Chem. Soc.*, **58**, 448 (1936).

²¹⁹ Thompson, H. W., *J. Chem. Soc.*, 790 (1934); *Proc. Roy. Soc.*, **150A**, 603 (1934); see also Thompson, H. W., and Frewing, J. J., *Nature*, **135**, 507 (1935).

²²⁰ Linnett, J. W., and Thompson, H. W., *Trans. Faraday Soc.*, **33**, 501, 874 (1937); see also Prileshaeva, N., and Terenin, A., *Ibid.*, **31**, 1483 (1935); *Acta Physicochim. U.R.S.S.*, **1**, 759 (1934); *Chem. Abs.*, **29**, 7798 (1935); Cunningham, J. P., and Taylor, H. S., *J. Chem. Phys.*, **6**, 359 (1938).

²²¹ Harms, J., and Jander, G., *Kolloid-Z.*, **77**, 267 (1936).

²²² Dufford, R. T., *J. Phys. Chem.*, **35**, 988 (1931); **37**, 709 (1933).

²²³ Gilman, H., and Heck, L. L., *Bull. soc. chim.*, **45**, 1095 (1929).

²²⁴ Müller, C., Frankenburger, W., and Grassner, F., *U. S. P.* 1,679,256, July 31, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **28**, 3669 (1928).

²²⁵ Reihlen, H., Gruhl, A., and von Hessling, G., *Annalen*, **472**, 268 (1929); *Brit. Chem. Abs.*, **1929A**, 1050.

of a mixture of ethyl mercaptan and an excess of iron pentacarbonyl greatly accelerates the reaction by which are formed hydrogen, carbon monoxide and *bis*-ironmercaptotricarbonyl:



A secondary reaction also occurs in which there is probably a slow decomposition of the *bis*-ironmercaptotricarbonyl to iron mercaptide.

With a mixture of equal volumes of the reactants at 3° to 5°C., the ratio of hydrogen to carbon monoxide evolved is 1:9.2. This is due to the reaction yielding instead of 4 molecules of carbon monoxide and one of hydrogen, three of carbon monoxide and one of formaldehyde, which is polymerized during the irradiation. In both of these cases, the primary reaction seems to be the loss of one molecule of carbon monoxide from two molecules of iron pentacarbonyl with the formation of $\text{Fe}_2(\text{CO})_9$, which then reacts with two molecules of the mercaptan to yield the *bis*-ironmercaptotricarbonyl and $\text{H}_2\text{C}_8\text{O}_8$. This latter product then breaks down to yield three molecules of carbon monoxide and one of hydrogen at the higher temperatures, or two molecules of carbon monoxide and formaldehyde at low temperatures.

When a mixture of one volume of iron pentacarbonyl and five of acetylacetone is irradiated at about 30° until evolution of gas ceases, the products formed are hydrogen, carbon monoxide, ferric acetylacetone and a substance which is probably an impure peroxide of ferrous acetylacetone. From 20 to 25 per cent of the carbonyl is unchanged. Nickel carbonyl and acetyl chloride react at 50° to 55°C., but the reaction is not affected by irradiation.

The decomposition of iron pentacarbonyl in toluene and alcohol may be sensitized by pinacyanol to wave-lengths longer than 6400 Å.²²⁶

²²⁶ Fedotov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **8**, 789 (1936); *Chem. Abs.*, **31**, 1702 (1937).

Chapter 25

Aromatic Compounds

Berthelot and Gaudechon¹ called attention to the stability of a number of typical aromatic compounds toward ultraviolet radiations. This is in general agreement with the stability of the aromatic nucleus toward heat and chemical reagents. A similar stability has also been noted in other cyclic compounds, such as pyrrole, furfural, pyridine and a few alkaloids. In substituents which may be present, however, may occur any of the types of photochemical change encountered in these substances when unattached to the benzene ring. When the double linkings in the ring have been saturated, as in hexahydrobenzene and piperidine, ultraviolet irradiation may cause decomposition. Cyclopropane, which does not absorb wave-lengths longer than 2000Å, undergoes a mercury-sensitized photopolymerization under the influence of the 2537Å line to a colorless oil of high boiling point.²

HYDROCARBONS

Berthelot³ found that benzene remains unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combined with oxygen, yielding resinous products, if placed over mercury. A brown sediment, derived from the thiophene present in the benzene, formed at the junction of the liquids.⁴

Benzene vapor exhibits a complex absorption spectrum, analyses of which have been given by Henri.⁵ The absorption of light produces only excited states, and most is reemitted as fluorescence. From the fluorescence spectrum, Almasy⁶ has drawn certain conclusions as to a predissociation of the molecule. Actually, however, little decomposition can be effected below about 600°C. by irradiation. With increasing temperatures, the fine structure of at least four of the bands of the benzene vapor spectrum successively disappears, and underlying continuous absorption increases. Henri and Cartwright suggested that incompletely separated molecules of C_6H_3 are formed by an excessive folding of the benzene ring, but that these recombine on cooling. This was proposed in an attempt to account for the predissociation spectra observed at higher temperatures.

In hexane, benzene exhibits a series of about seven relatively broad bands.⁷ Kwieninski and Marchlewski⁸ locate the maxima of six bands at 2648, 2608, 2546,

¹ Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).

² Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

³ Berthelot, D., *Ann. Chim. Phys.*, **19**, 150 (1900).

⁴ *J. Soc. Chem. Ind.*, **47**, 727 (1928); *Report of Joint Research Committee of the National Benzol Association, and the University of Leeds*, 237 (1928).

⁵ Henri, V., *J. phys. Radium*, **3**, 181 (1922); Henri, V., and Cartwright, C. H., *Compt. rend.*, **200**, 1532 (1935); Kistiakowsky, G. B., and Solomon, A. K., *J. Chem. Phys.*, **5**, 609 (1937).

⁶ Almasy, F., *Naturwiss.*, **20**, 296 (1932); Almasy, F., and Shapiro, C. V., *Z. physik. Chem.*, **25B**, 391 (1934); Kistiakowsky, G. B., and Nelles, M., *Phys. Rev.*, **41**, 595 (1932).

⁷ Klingstedt, F. W., *Compt. rend.*, **175**, 1065 (1922); see also Orndorff, W. R., Gibbs, R. C., McNulty, S. A., and Shapiro, C. V., *J. Am. Chem. Soc.*, **50**, 831 (1928); Shapiro, C. V., and Gibbs, R. C., *Phys. Rev.*, **31**, 310 (1928).

⁸ Kwieninski, L., and Marchlewski, L., *Bull. Acad. Polonaise*, **A**, 255 (1929); *Chem. Abs.*, **24**, 783 (1930).

2490, 2433 and 2390A. The spectrum is of importance because it frequently appears in the absorption spectra of other not especially purified compounds of which benzene is a contaminant. As such, it has been erroneously reported as the absorption spectrum of substances, such as ether, contaminated by it. Indeed, the presence of small amounts of benzene vapor in the atmosphere can be detected and the benzene determined by drawing the air through alcohol and then taking the absorption spectrum. As little as 0.1 mg. per liter of air can be determined with an accuracy of about 5 per cent (in the absence of homologs) in a one liter sample.⁹

The absorption of the homologs of benzene has also been extensively studied.¹⁰ In general, the addition of alkyl groups into benzene leads to a fusion, more or less complete, of the benzene bands.

Kailan¹¹ compared the action of radium and of ultraviolet rays upon toluene. The former changed less than 0.25 per cent of a sample of toluene exposed for two years. The products formed included benzaldehyde, benzoic acid, and apparently, formic acid. The principal product consisted, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde. Changes of a similar nature and order of magnitude were said to have been produced by 22 hours of exposure to the radiation from a quartz mercury lamp at a distance of 8 to 9 centimeters. In the presence of water, the action was slightly increased and some oxalic acid was also formed.

The fact that the most easily isolable products of the autoxidation in light of benzene homologs are carboxy-acids was attributed by Suida¹² to the relative stability of intermediate products. He believed that, with the quartz lamp as source, the velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation, estimated by the liberation of iodine from acidified potassium iodide. The amount of carboxylic acid formed could not, however, be entirely due to the decomposition of peroxide. More recent workers have contributed to this work, but an understanding of the mechanism of the process is not complete.

The oxidation of xylene occurs more than twice as rapidly as that of toluene, para-xylene oxidizing more rapidly than the ortho isomer. The process is accelerated by the addition of small quantities of nitrobenzene, or of one of the nitro-toluenes.

According to Sudborough, Watson and Narayanan¹³ it was claimed by Eckert¹⁴ that 40 per cent yields of benzoic acid could be obtained in six weeks from toluene by atmospheric oxidation in sunlight in the presence of anthraquinone. In a repetition and extension of these experiments, Sudborough and co-workers used 200-cc. quartz flasks containing 50 gm. of toluene and 5 gm. of anthraquinone. The flasks were filled with oxygen and connected with a reservoir of that gas.

⁹ Laurian, P., *14me Congr. chim. ind. Paris*, Oct. 1934, 6 pp; *Chem. Abs.*, **29**, 6173 (1935). For data on the absorption of solid benzene, see Fringsheim, P., *Physik. Z.*, **27**, 856 (1926). Kronenberger, A., and Fringsheim, P., *Z. Physik*, **40**, 75 (1926). For the Schumann region, see Price, W. C., and Wood, R. W., *J. Chem. Physics*, **3**, 439 (1935).

¹⁰ Pestemer, M., and Gubitz, O., *Monatsh.*, **64**, 426 (1934); Henri, V., and Walter E., *Compt. rend.*, **176**, 746 (1923); Conrad-Billroth, H., *Z. physik. Chem.*, **B29**, 170 (1935); Wolf, K. L., and Herold, W., *Z. physik. Chem.*, **B13**, 210 (1931); **B21**, 389 (1933); Radulescu, D., and Dragulescu, C., *Physik. Z.*, **36**, 66 (1935). Aubert, M., and Gheorghiu, T., *Ann. combustibles liquides*, **8**, 451 (1933); *Chem. Abs.*, **29**, 2448 (1935). Ramart-Lucas, Mme., and Amagat, P., *Compt. rend.*, **188**, 638 (1929); *Bull. soc. chim.*, **51**, 108 (1932); Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 135 (1934).

¹¹ Kailan, A., *Monatsh.*, **40**, 445 (1920); *J. Chem. Soc.*, **118**, i, 538 (1920).

¹² Suida, H., *Monatsh.*, **33**, 1255 (1912).

¹³ Sudborough, J. J., Watson, H. E., and Narayanan, B., *J. Indian Inst. Sci.*, **8A**, 1 (1925); British P. 182,487; *J. Soc. Chem. Ind.*, 782 (B.1925); John, H., *Ber.*, **58B**, 1563 (1925).

¹⁴ Eckert, A., *Indian P.* 8425; *Ber.*, **58B**, 313 (1925).

They were rocked at such a rate that the liquid was continuously splashed over the upper part of the interior surface exposed to the light. The temperature was 63-6°C. when the source was a mercury arc and 29-50°C. when sunlight was employed. The amount of acid determined by titration always exceeded that which could be isolated as benzoic acid, probably because of the formation of some formic acid. The amount of acid formed was roughly proportional to the time of exposure and was markedly dependent upon the amount of water present. The yield of acid in sunlight ranged from 0.76 per cent with 2.5 gm. water and 2.03 per cent with 25 gm. of water after 60 hours to 6.60 and 17.3 per cent, respectively, after 400 hours. In ultraviolet light, the values were: after 200 hours, 4.7 per cent with 2.5 gm. water and 15.7 per cent with 25 gm. water and, after 600 hours 16.3 and 34.7 per cent. The addition of nitrobenzene as catalyst had practically no effect. The presence of oxygen was essential. Meta-xylene and mesitylene showed no marked oxidation after 200 hours of ultraviolet treatment. It was found by Castiglioni¹⁵ that one and a half times as much benzoic acid was formed in a given time when Uviol flasks were used as when ordinary glass flasks were employed.

The discrepancy between the reports regarding the effect of nitrobenzene may have been due to a slow photoreaction between toluene and nitrobenzene which occurs even under nitrogen and in the absence of anthraquinone. Vecchiotti and Zanetti¹⁶ find that a large quantity of nitrobenzene (100 gm.) and 20 gm. of toluene give, after six months in sunlight, 20 gm. of benzoic acid and *p*-aminophenol. This indicates that the side-chain of the toluene is oxidized and that the nitrobenzene is reduced to aminophenol. This reaction had been observed previously by Ciamician and Silber.¹⁷

Subsequent observations of the anthraquinone-sensitized oxidation of toluene by Kothari and Watson¹⁸ indicated the rate to be greatest in the presence of 1 per cent of catalyst. The rate is initially slow, but gradually speeds up and eventually becomes constant. They believed the fraction of toluene oxidized, 8.3 to 9.8 per cent, to be larger in proportion to time when the sun was the source than when the mercury arc was employed. Uranium salts had irregular effects as catalysts.¹⁹

Xylene mixed with an aromatic nitro-hydrocarbon is reported to contain more active oxygen after exposure to light and oxygen than pure xylene exposed to light and oxygen, but Suida²⁰ found that the presence of a nitro-compound reduced the total yield of oxidation product, although considerable quantities of toluic aldehyde were present. Thus in the presence of a nitro-hydrocarbon the less stable products of oxidation (aldehydes and peroxides) remained, while the pure chemical reaction (the decomposition of these primary products to the next higher and more stable stage of oxidation) was delayed. It was possible by cooling in carbon dioxide and ether to bring almost to a standstill the decomposition of the benzene hydroperoxide (formed from benzaldehyde by the action of ultraviolet). The product of the primary autoxidation process could not be isolated, as it decomposed into benzoic acid within a few minutes after removing it from

¹⁵ Castiglioni, A., *Gazz. chim. ital.*, **63**, 818 (1933); *Brit. Chem. Abs.*, **A**, 264 (1934); see, however, John, H., *Ber.*, **58B**, 1563 (1925); *Chem. Abs.*, **20**, 337 (1926).

¹⁶ Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60**, 479 (1930); *Chem. Abs.*, **25**, 251 (1931).

¹⁷ Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33**, 354 (1903); **36**, 174, 176, 190, 197 (1906).

¹⁸ Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14**, 11 (1931); *Chem. Abs.*, **26**, 378 (1932).

¹⁹ See also Nozicka, F., U. S. P. 1,945,067, Jan. 30, 1934; *Chem. Abs.*, **28**, 2273 (1934); German Patent 624,964; *Chem. Abs.*, **30**, 4870 (1936); and Kreidl, I., U. S. P. 1,971,042, Aug. 21, 1934, for other catalysts related to anthracene or anthraquinone.

²⁰ Suida, H., *Ber.*, **47**, 467 (1914); *Monatsh. Chem.*, **33**, 1268 (1912).

the cooling mixture. Little is known as yet regarding the mechanisms of these oxidations.

Plotnikow²¹ notes that sunlight acts on solutions of potassium dichromate containing various organic compounds. Triphenylmethane is unaltered and benzene remains almost unchanged even in the presence of ferric chloride, but toluene yields a variety of products. Phenol forms benzoquinone and a mixture of polyhydric phenols. Ortho- and meta-xylenes yield tolualdehydes and acids, and some formic acid is formed from *p*-xylene. Quinol forms primarily benzoquinone, but phthalic acid also has been isolated from the reaction products. Resorcinol and pyrocatechol yield trihydric phenols, benzoquinone and similar compounds. A solution containing *o*-cresol decomposes with evolution of carbon dioxide and separates into two layers, of which the lower contains unchanged cresol, chromic hydroxide, and a tarry substance, and the upper, benzoic and oxalic acids. Naphthalene and α -naphthol are unchanged after ten months of irradiation. Some aniline dyes give fluorescent solutions. Aniline is converted rapidly into aniline black, and *p*-aminophenol into benzoquinone and ammonia. Results with pseudocumene indicate that the possibility of terpene formation is dependent on a symmetrical molecular structure. Dihydroxyanthraquinone breaks down into benzoquinone and carbon dioxide. Mixtures of isopulegol and ammonium dichromate in various proportions yield on irradiation in aqueous or alcohol solutions only about 1 per cent of isopulegone, whereas isoeugenol undergoes extensive oxidation.

Substitution Products of Benzene. Although the absorption spectra of the various halogen substitution products of benzene and its homologs have been recorded and in some cases analyzed,²² little is known regarding their photochemical decompositions or reactions.

Without catalysts, *p*-bromobenzenesulfonate undergoes no decomposition in darkness and less than 2 per cent in light.²³ In the presence of charcoal, 0.65 to 0.95 per cent decomposition occurred in darkness and 2.28 to 3.21 per cent in the light of a carbon arc. The corresponding values in the presence of copper were 3.78-5.26 and 5.83-7.79 per cent. In the presence of both copper and charcoal, the values were 10.71 to 23.70 per cent decomposed in darkness and 14.29 to 26.28 per cent in light.

PHOTOCHEMICAL NITRATIONS AND NITRO- COMPOUNDS

In the photochemical reaction in sunlight between benzene and a mixture of nitric and sulfuric acids, Sollazzo²⁴ finds that there are successively formed nitrobenzene, nitrosobenzene, azoxybenzene and finally the salts of azoxybenzenesulfonic acid.

Bass and Johnson²⁵ allowed nitrogen peroxide to react with benzene for three months in sealed tubes both in darkness and in sunlight. The only nitration products identified were the mono- and di-nitroderivatives, formed in very small yield. Anhydrous nitrogen peroxide gas was passed over 50 gm. of dry toluene in a water-cooled quartz tube exposed to a quartz mercury arc for six hours. In addition to 2.5 gm. of benzoic acid and 32.0 gm. of toluene, there was obtained 13.0 gm. of an unstable low-boiling (40-80°C.) liquid which showed no definite boiling point, but decomposed into toluene and nitrogen peroxide. They believed the nitrogen peroxide to act solely as an oxidizing agent, practically no nitration taking place.

²¹ Plotnikow, J., *Chem. Ztg.*, **52**, 669 (1928); *Chem. Abs.*, **22**, 4380 (1928).

²² Errera, J., and Henri, V., *J. Phys. Radium*, **9**, 205, 249 (1928); Conrad-Billroth, H., *Z. physik. Chem.*, **B19**, 76 (1932); **B25**, 139, 217 (1934); Klingstedt, F. W., *Z. physik. Chem.*, **20B**, 125 (1933).

²³ Sandomnini, C., *Atti R. Accad. Lincei*, **2**, 427 (1925); *Chem. Abs.*, **20**, 1018 (1926).

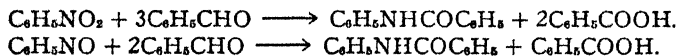
²⁴ Sollazzo, G., *Officina*, **4**, 268 (1931); *Chem. Abs.*, **26**, 1862 (1932).

²⁵ Bass, I. W., and Johnson, T. B., *J. Am. Chem. Soc.*, **46**, 456 (1924).

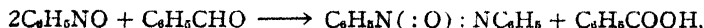
More recently, however, it was found²⁶ that when 40 gm. of toluene were passed in vapor form with 180 to 200 gm. of nitrogen peroxide and 45 to 50 liters of carbon dioxide at 14° to 15°C. during two hours before or through a jacketed quartz mercury-vapor lamp, 55 per cent of the toluene reacted, giving about 5 gm. of the side-chain nitration product, and 27-28 gm. of a mixture of mononitrotoluenes. No dinitrotoluene and no benzoic acid were produced. Raising the temperature to 58-60°C. did not affect the side-chain nitration, but lowered the yield of the nitrotoluenes to 15 gm. In the absence of radiation, less toluene reacted, but the relative amounts of side-chain and nuclear substitution were but little affected. The nitration of benzene was but little affected by irradiation. Titov and Baryshnikova²⁷ obtained rather similar results under conditions, such as low concentration and illumination, which favored the dissociation of the N_2O_4 . They did observe a considerable amount of disubstitution in the side chain, as well as some benzaldehyde and benzoic acid formation. These products were secured in the absence of illumination. In sunlight or the light of the mercury arc, all the reactions were accelerated except that the ring substitution was reduced approximately 4 to 9 per cent.

Irradiation has little effect on the nitration of benzene, *n*-hexane or cyclohexane. In general, it is helpful only when the completely symmetrical structure of the benzene molecule is disturbed by the presence of a side-chain.²⁸

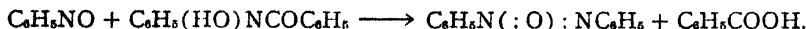
To obtain information regarding the photochemical action of nitrobenzene on various organic compounds, a field already investigated by Ciamician and Silber,²⁹ Vecchiotti and Zanetti³⁰ exposed it in an atmosphere of nitrogen to sunlight for six months in contact with the substance to be tested. In the reaction with cinnamic acid, the products obtained included benzoic acid, carbon dioxide, benzanilide, azoxybenzene and hydroxyazobenzene. It was assumed that the double bond of the cinnamic acid was ruptured, with the formation of benzaldehyde and $OHCCOOH$, these products being oxidized to benzoic and oxalic acids. On further oxidation, cinnamic acid yields carbon dioxide. The nitrobenzene is reduced to nitrosobenzene. The formation of the remaining three compounds is accounted for by reference to the explanation given by Ciamician and Silber³¹ for the action of nitrobenzene on benzaldehyde. Benzanilide may be formed from benzaldehyde by either of the reactions:



Azoxybenzene may be formed by



or by analogy with the Bamberger^{31a} reaction of nitrosobenzene and C_6H_5HNOH by



²⁶ Schorigin, P., and Toptschiev, A., *Ber.*, **67**, 1362 (1934); *J. Gen. Chem. Russ.*, **5**, 549 (1935), *Brit. Chem. Abs.*, **A**, 61 (1936).

²⁷ Titov, A. I., and Baryshnikova, A. N., *J. Gen. Chem. U.S.S.R.*, **6**, 1801 (1936); *Chem. Abs.*, **31**, 4285 (1937).

²⁸ Schorigin, P., and Toptschiev, A., *loc. cit.*, for attempts at substitution of hydrocarbons by $NOCl$ during irradiation, see Perrot, R., *Compt. rend.*, **198**, 1424 (1934).

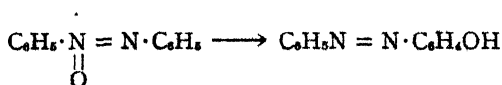
²⁹ Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33**, 354 (1903); **36**, 174, 176, 190, 197 (1906).

³⁰ Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60**, 479 (1930); *Chem. Abs.*, **25**, 251 (1931).

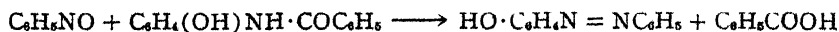
³¹ Ciamician, G., and Silber, P., *Compt. rend. Acad. Lincei*, **14**, 265 (1905).

^{31a} *Ber.*, **35**, 1606 (1902).

The last of the three compounds may be formed from $C_6H_5N(:O):NC_6H_5$ by transposition.⁸²



or by



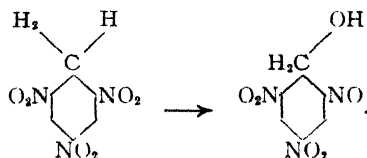
Even in darkness, cinnamic acid and nitrobenzene gave benzoic acid and azoxybenzene.

In the photochemical reaction of nitrobenzene and naphthalene, a trace of β -naphthol was the only product identified.

On exposure to sunlight, Sollazzo³³ found a mixture of ethanol, ammonium hydroxide and *m*-dinitrobenzene to become red-yellow. In the case of amyl alcohol, the color was cherry-red; it was permanent in darkness.

Illumination of 1-styryl-3-bromostyryl-4, 6-dinitrobenzene gives 2-phenyl-5-styryl-6-nitroisatogen.⁸⁴

Molinari and Giua are said³⁵ to have observed 2,4,6-trinitrotoluene to turn slowly brown on the surface when exposed to bright daylight. The melting point dropped from 80° to 74° in three months. Custis³⁶ found that a more rapid reaction occurs when the material was exposed to an iron arc, but a mercury arc did not prove effective. Schultz and Ganguly³⁷ attribute the red coloration observed after the prolonged action of light on 2,4,6-trinitrotoluene in the presence of oxygen, hydrogen, nitrogen or *in vacuo*, to the production of two tautomeric quinonoximes, $C_7H_5O_6N_3$, of melting points above 280°C. They can be separated by their differing solubilities in cold acetone. Each dyes wool red. They are considered to be 2-nitro-6-nitroso-5-hydroxymethyl-*p*-benzoquinone-4-oxime and 2-nitro-4-nitroso-5-hydroxymethyl-*o*-benzoquinone-2-oxime. The course may involve the migration of an oxygen atom from a nitro- group to the methyl group, as in



In acetone solution, the process may stop here, the product melting at 108-111°C. In the case of the solid, a repetition of the process yields the unstable 4-nitro-2,6-dinitrosodihydroxymethylbenzene. One hydroxyl migrates to the nucleus, and then passes its hydrogen to one or the other nitroso- group, forming the *o*- and *p*-oximes. The assumption that only the nitro- groups in the 2 and 6 positions are reduced is supported by the observation that 2,6-dinitrotoluene is converted by exposure to light into a yellow substance, probably 2,6-dinitroso-4-hydroxybenzyl

⁸² Knipscheer, H. M., *Rec. trav. chim.*, **22**, 14 (1903).

³³ Sollazzo, G., *Officina*, **4**, 340 (1931); *Chem. Abs.*, **26**, 3729 (1932); *Boll. chim. farm.*, **72**, 913 (1933); *Brit. Chem. Abs.*, **A**, 264 (1934); *Chem. Abs.*, **28**, 5758 (1934).

⁸⁴ Ruggli, P., and Zimmerman, A., *Helv. Chim. Acta*, **15**, 865 (1932); *Chem. Abs.*, **27**, 292 (1933).

³⁵ Escalés, R., "Die Explosivstoffe mit besonderer Berücksichtigung der neueren Patente." *Heft*, **6**, "Nitrosprengstoffe," p. 295. Leipzig. Vereinig. wissenschaft. Verleger, 1915.

³⁶ Custis, H. H., *J. Frank. Inst.*, **184**, 876 (1917); *Chem. Trade J.*, **62**, 90; *Chem. Zentr.*, 208, 1 (1928).

³⁷ Schultz, G., and Ganguly, K. L., *Ber.*, **58B**, 702 (1925).

alcohol, although *p*-nitrotoluene is completely unchanged. The presence of a nitro-group in the *para* position appeared to retard the change, since 2,4-dinitrotoluene is almost stable to light. 2,4,6-Trinitrobenzyl alcohol in benzene and 2,4,6-trinitrobenzyl bromide, as a solid or in benzene, are also sensitive to light.

It was believed by Krauz and Turek³⁸ that exposure of trinitrotoluene in thin layers to sunlight increased its sensitiveness to shock. This was attributed to a decomposition leading to the formation of both picric and trinitrobenzoic acids. Metals or metal oxides were supposed to hasten this change, which occurred to a sufficient extent to change the melting point in four months from 81.4° to 73.5°C. These results have been critically examined by Wichart and Donat³⁹ and by Lodati,⁴⁰ who find the technical products completely stable in contact with metals. The latter worker states, however, that in diffused light, the compound formed some nitrous vapors in three months.⁴¹

According to Sachs and Hilpert,⁴² the nitrobenzylidene group should be light-sensitive. This was confirmed by I. and H. Tănăsescu⁴³ in studies of the action of sunlight on *o*-nitrobenzylideneglycol, $\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}(\text{H}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, which yielded a white crystalline isomer *o*-NO-C₆H₄-C(OH)(OCH₂)₂CH₂O, melting at 128°C. to a green liquid which readily hydrolyzed on boiling with acid or base to form glycol and *o*-nitrosobenzoic acid. A similar migration of oxygen from a nitro-group to form an alcohol group (mentioned by Schultz and Ganguly in the case of trinitrotoluene) was observed in di-*o*-nitrobenzylidencerythritol. A similar type of behavior is also encountered in the case of *o*-nitrobenzaldehyde. Tănăsescu and Macovski⁴⁴ have extended this work to include the changes in 1,2,5,6-di-*o*-nitrobenzylidenedulcitol which gives a resin, possibly by partial isomerization and *p*-nitrobenzylidene-3-benzoylglycerol. Included are also the *o*-nitrobenzylideneacetals of a number of other glucides, such as mannitol and sorbitol. The structure of the photochemical isomerization products was not definitely established, these authors believing an open-chain formula of the type $\text{O} \cdot \text{ROCH}_2\text{CH}_2\text{OCOC}_6\text{H}_4\text{NO}$ the most adequate. Recently, the corresponding compounds of galactose, α -methyl-galactose, mannose, rhamnose, fructose, lactose and sucrose have been found to give isomerizations when irradiated in chloroform and benzene solutions.⁴⁵

BENZALDEHYDE

Although benzaldehyde is thermally decomposed only at temperatures of 400°C. and higher, wave-lengths shorter than 2600Å (more accurately 2438Å) produce a photolysis at room temperature, according to de Hemptinne.⁴⁶ He believed the primary products to be carbon monoxide, a phenyl radical and a hydrogen atom, the latter combining to produce benzene. The energy necessary for this was cal-

³⁸ Krauz, C. and Turek, O., *Z. ges. Schiess- u. Sprengstoffw.*, **20**, 49 (1925); *Chem. Abs.*, **19**, 2747 (1925); *Chem. Age (London)*, **13**, 392 (1925); *Chem. Abs.*, **20**, 824 (1926)

³⁹ Wichart and Donat, *Z. ges. Schiess- u. Sprengstoffw.*, **20**, 69 (1925)

⁴⁰ Lodati, D., *Giorn. Chim. Ind. Appl.*, **7**, 572 (1925); *Chem. Abs.*, **20**, 3815 (1926); but see also, Sucharevskii, M., *Z. ges. Schiess- u. Sprengstoffw.*, **20**, 40 (1927); *Chem. Abs.*, **21**, 3462 (1927)

⁴¹ For spectriographic studies of this reaction, see also Pavlik, M., *Chimie et Industrie, Special No.*, 245 (June, 1933)

⁴² Sachs, F., and Hilpert, S., *Ber.*, **37**, 3125 (1904).

⁴³ Tănăsescu, I., and Tănăsescu, H., *Bul. soc. stiinte Cluj*, **2**, 369 (1925); *Chem. Abs.*, **20**, 749 (1926).

⁴⁴ Tănăsescu, I., and Macovski, E., *Bull. soc. chim.*, **53**, 1097 (1933); *Chem. Abs.*, **28**, 1330 (1934), *Bull. soc. chim.*, **51**, 1371 (1932); *Chem. Abs.*, **27**, 1874 (1933), *Bull. soc. chim.*, **51**, 1556 (1932), *Chem. Abs.*, **27**, 2142 (1933), *Bull. soc. chim.*, **45**, 1022 (1929); *Chem. Abs.*, **24**, 2118 (1930); *Bull. soc. chim.*, **47**, 86 (1930), *Chem. Abs.*, **24**, 2429 (1930); *Bull. soc. chim.*, **47**, 457 (1930); *Chem. Abs.*, **24**, 4270 (1930).

⁴⁵ Tănăsescu, I., and Craciunescu, E., *Bull. soc. chim.*, **3**, 581 (1936); Tanasescu, I., and Jonescu, M., *Bull. soc. chim.*, **3**, 1517 (1936).

⁴⁶ de Hemptinne, M., *Compt. rend.*, **186**, 1295 (1928); *Ann. Soc. Sci. Bruxelles*, **48B**, 98 (1928), *Brit. Chem. Abs.*, **A**, 409 (1929); *J. Phys. Radium*, **9**, 357 (1928).

culated to be 115.7 kcal., corresponding to 2461Å, at which the "total" absorption band of the benzaldehyde spectrum begins.

The absorption spectrum has been studied recently by Almasy⁴⁷ who found three broad regions. From 3747 to 3163Å, there were 159 measurable bands in the vapor; between 2963 and 2599Å there were 51. At 2428 to 2349, there were six bands followed by continuous absorption. As the temperature is raised, the character of the spectrum is altered, the narrow bands fusing into broader ones indicating the occurrence of predissociation at longer wave-lengths, the higher the temperature. At 208°C the fine bands present at lower temperatures between 2966 and 1610Å are continuous and radiations in this range produce photolysis. At 270°C radiations shorter than 3200Å produce dissociation.

On exposure to ultraviolet rays, hexahydrobenzaldehyde yields carbon monoxide, cyclohexane and the dimer.⁴⁸ Phenylacetaldehyde does not evolve carbon monoxide, but is partly converted into a yellow oil and a brownish-red, viscous residue. Hydrocinnamaldehyde also is said to be practically unaffected by ultraviolet light. Hexahydrophenylacetaldehyde yielded a gas containing 88 per cent of carbon monoxide, hexahydrotoluene, and small quantities of polymerized products.⁴⁹ Hexahydro-β-phenylpropaldehyde, after ten hours' exposure to ultraviolet, gave carbon monoxide more slowly and in smaller quantity and highly polymerized products from which only a trimer of the original aldehyde, but no hexahydro-ethylbenzene, could be isolated.

Oxidation of Benzaldehyde It was early claimed⁵⁰ that the autoxidation of either benzaldehyde or of pinene under the influence of rays from a Uviol lamp increased the electrical conductivity of oxygen. It had been found by Jorissen and Ringer⁵¹ that when a mixture of one mole of benzaldehyde and two of acetic anhydride is exposed to the diffused light of an arc or a magnesium flame in an atmosphere of oxygen in a closed vessel, benzoylacetol peroxide could be obtained.

Suida⁵² passed a current of oxygen through a solution of benzaldehyde in petroleum ether (cooled with ice), while irradiating it by a Heraeus quartz lamp at a distance of two centimeters. After six hours a considerable amount of benzoic acid and small quantities of a peroxide were found, which could not be readily isolated. When the vessel was cooled by means of solid carbon dioxide and ether, the formation of the peroxide was much increased and a white deposit with strong oxidizing properties and a pungent odor was obtained.

By a combination of iodometric and acidimetric titrations during the reaction, Bäckström⁵³ found that perbenzoic acid is the product of the photochemical reaction. The quantum efficiency is high, of the order of 10,000. The reaction can be inhibited. The perbenzoic acid subsequently reacts with benzaldehyde, forming benzoic acid by a pseudo-unimolecular thermal reaction, which shows little or no negative catalysis. This reaction is accelerated by light, but the quantum yield is less than 0.5 per cent of that of the reaction by which the perbenzoic acid is formed. The quantum yield for the total reaction, measured by the oxygen uptake, decreases during the progress of the reaction.

⁴⁷ Almasy, F., *J. chim. phys.*, **30**, 528, 713 (1933).

⁴⁸ Franke, A., and Sigmund, F., *Monatsh.*, **46**, 61 (1925); cf. also Wallach, O., and Isaac, E., *Annalen*, **347**, 331 (1906).

⁴⁹ Sigmund, F., *Monatsh.*, **52**, 185 (1929).

⁵⁰ Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12**, 93 (1915); *J. Chem. Soc.*, **108** (ii), 80 (1915).

⁵¹ Jorissen, W. P., and Ringer, W. E., *Chem. Weekblad*, **2**, 19; *Chem. Zentr.*, **76**, 817 (1905).

⁵² Suida, H., *Ber.*, **47**, 471 (1914).

⁵³ Bäckström, H., *Med. K. Vetenskapsakad. Nobelinst.*, **6**, Nos 15 and 16 (1927); Bäckström, H., and Beatty, H. A., *J. Phys. Chem.*, **35**, 2530 (1931).

According to Kothari and Watson⁵⁴ this decrease, which is found also in toluene solutions and by the use of an incandescent light source, is greater than could be accounted for by the retarding action of the benzoic acid. It was less when benzene was the solvent. Anthraquinone may serve as an accelerator of the reaction when toluene is the solvent, but is not effective in benzene. Benzoquinone is a strong inhibitor, and phenolic compounds also act in this way. According to Jorissen and Dekking,⁵⁵ the photooxidation of benzaldehyde in the presence of iodobenzene induces oxidation of the latter compound.

Photochemical reactions between aldehydes and quinones have been the subject of a number of empirical observations.⁵⁶ Angeletti and Baldini,⁵⁷ found that after exposure to sunlight for six months an equimolar mixture of benzaldehyde and toluquinone in benzene gave benzoic acid, toluhydroquinone, a relatively small quantity of diethyl toluhydroquinone benzoate, an unidentified phenolic compound, and large quantities of resins. Light reduced the toluquinone to toluhydroquinone and oxidized the benzaldehyde to benzoic acid. The latter then esterified the two hydroxyl groups of toluhydroquinone. Cinnamaldehyde and toluquinone similarly gave cinnamic acid, toluhydroquinone and a monocinnamate of toluhydroquinone.⁵⁸ No compounds corresponding to the 2,5-dihydroxybenzophenone were reported by Klinger.⁵⁹

It has been stated by Chattaway⁶⁰ that benzaldehydephenylhydrazone reddens slowly in diffused light. In sunlight, the change becomes very noticeable in a few minutes, reaching, in a few hours, a maximum intensity, the crystals having a brilliant scarlet color like that of azobenzene. The change could be produced also by the light of an iron arc, but the ultraviolet rays were not held responsible since the interposition of glass did not interfere with the effect. Hodgson and Handley⁶¹ found no change in the phenylhydrazone of *p*-nitrobenzaldehyde under similar treatment.

Transformation of o-Nitrobenzaldehyde. The nature of the isomerization which occurs when this compound is irradiated either as a solid or in acetone solution is similar to that described on page 472 for the *o*-nitrobenzylidene glycols. An oxygen atom is removed from the nitro- group and transferred to the aldehyde group, forming in this case *o*-nitrosobenzoic acid. Weigert and Kummerer⁶² showed that the amount of the reaction is proportional to the time of irradiation. In experiments in which the intensity was varied, they believed that their data indicated a slight deviation from the Bunsen-Roscoe law. When ultraviolet light was employed, the rate of the change was independent of the concentration, but when violet light was used the rate was at first proportional to the concentration.

In later work, the quantum yield was found⁶³ to be 0.5 when the wave-lengths 4360, 4050 or 3660Å were used. To account for this, they developed a special theory in which the orientation of the molecules with respect to the electric vector

⁵⁴ Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14**, 11 (1931); *Chem. Abs.*, **26**, 378 (1932).

⁵⁵ Jorissen, W. P., and Dekking, A. C. B., *Rec. trav. chim.*, **57**, 829 (1938).

⁵⁶ Ciamician, G., and Silber, P., *Ber.*, **24**, 1430 (1891); **31**, 124 (1898); Klinger, H., *Annalen*, **249**, 137 (1888); Bargellini, G., and Monti, L., *Gazz. chim. ital.*, **60**, 474 (1930); *Chem. Abs.*, **25**, 96 (1931).

⁵⁷ Angeletti, A., and Baldini, V., *Gazz. chim. ital.*, **64**, 346 (1934); *Chem. Abs.*, **28**, 5422 (1934).
⁵⁸ Angeletti, A., *Atti accad. sci., Torino, Classe sci. fis. mat. nat.*, **70**, 326 (1935); *Chem. Abs.*, **30**, 1383 (1936); *Atti V Congr. Naz. Chim.*, **1**, 280 (1936); *Brit. Chem. Abs.*, **A** (II), 196 (1937).

⁵⁹ Klinger, H., *Annalen*, **382**, 211 (1911); *Chem. Abs.*, **5**, 3456 (1911).

⁶⁰ Chattaway, F. D., *J. Chem. Soc.*, **89**, 463 (1906).

⁶¹ Hodgson, H. H., and Handley, F. W., *J. Chem. Soc.*, 1882 (1928).

⁶² Weigert, F., and Kummerer, L., *Ber.*, **46**, 1207 (1913); see also Bowen, E. J., Hartley, H., Scott, W. D., and Watts, H. G., *J. Chem. Soc.*, **125**, 1218 (1924).

⁶³ Weigert, F., and Brodmann, L., *Trans. Faraday Soc.*, **21**, 453 (1926).

of the incident light was considered a determining factor. It was suggested that the transfer of an oxygen atom to an aldehyde group takes place only when the electric vector of the incident radiation corresponds to the line between the nitro- and aldehyde groups. It could be shown that only 50 per cent of the molecules would be so oriented as to react. Thus, for these molecules, the quantum yield would be unity, although the observed value was but 0.5. Such a theory lost its significance when it was found that many reactions in solutions have quantum yields varying in exact value, but less than unity. Furthermore, it has been found by some that Weigert's results⁶⁴ showed some variations from the 0.5 which his theory demands, as various wave-lengths were employed. This, however, has been denied by Weigert and Pruckner⁶⁵ after further observations. The value of 0.5 has been verified also by Leighton and Lucy⁶⁶ for 2,4-dinitrobenzaldehyde as well as for *o*-nitrobenzaldehyde. They found somewhat higher values in the case of 2,4,6-trinitrobenzaldehyde.⁶⁷ These, as well as other recent workers⁶⁸ reject the Weigert theory, and believe the usual explanations given for low quantum yields in liquid or solid-phase reactions to apply. Leighton and Lucy related the yield of 0.5 to the assumption that the N=O adjacent to the aldehyde group must be excited for the transformation to occur. They consider the processes of energy exchange between the two N=O linkings.

Janssen found the absorption spectrum of the vapor of this compound to be continuous, implying a primary photodecomposition. Zimmer, who noted the compound to be dichroic at 4360 and 4050Å although not a mixture of two tautomers, found it to exhibit no appreciable fluorescence. He believed that the primary process produces nitrosobenzaldehyde and an oxygen atom. The latter could recombine with the other dissociation product in either of two ways—to restore the original compound or to form the nitrosobenzoic acid. The equal likelihood of these two processes would account for the quantum yield of 0.5. Küchler and Patat⁶⁹ found the quantum yield in the gas phase to be much higher than that in solution. At 90°C., it reached 0.75, but could be lowered to 0.5 by the presence of 700 mm. nitrogen. They did not accept the theory of a primary splitting off of oxygen and could find no evidence for the primary formation of oxygen atoms. Neither free oxygen nor nitric oxide was formed. They believed the simplest explanation of the quantum yields of 0.5 to be a deactivation of some type of excited molecule, regulated intramolecularly.

Various other compounds, as has already been indicated, undergo a similar type of transformation. Tănăsescu⁷⁰ believes all substances which contain the *o*-nitrobenzaldehyde grouping and which are light-sensitive contain a mobile hydrogen atom. An example of a light-insensitive compound is *o*-nitrocinnamaldehyde. In this case, according to Kögel, the aldehyde group differs in not being an oxygen-acceptor.⁷¹ In the presence of pyrogallol as oxygen acceptor, however, the nitro- group of this aldehyde, as well as that of *o*-nitrobenzaldehyde, is light-

⁶⁴ Weigert, F., and Pruckner, F., *Z. physik. Chem. Bodenstein-Festband*, 775 (1931); Weigert, F., (1929).

⁶⁵ Leighton, P. A., and Lucy, F. A., *J. Chem. Physics*, 2, 756, 760 (1934).

⁶⁷ See also Secareanu, S., and Lupas, I., *Bull. soc. chim.*, 3, 1161 (1936); *Brit. Chem. Abs.*, A, 986 (1936).

⁶⁸ Wegscheider, R., *Monatsh.*, 52, 68 (1929); Janssen, C., *Z. physik. Chem.*, B18, 241 (1932); Zimmer, K. G., *Ibid.*, B23, 239 (1933); Bowen, E. J., *Trans. Faraday Soc.*, 21, 523 (1926).

⁶⁹ Küchler, L., and Patat, F., *Monatsh.*, 68, 275 (1936); *Z. Elektrochem.*, 42, 529 (1936).

⁷⁰ Tănăsescu, I., *Bull. soc. chim.*, 39, 1443 (1926).

⁷¹ Kögel, J., *Z. wiss. Phot.*, 24, 216 (1926); *Chem. Abs.*, 20, 3646 (1926).

sensitive. In the case of nitroterephthaldehyde, the maximum quantum yield in the transformation into 2,4,1-nitrosoterephthaldehydic acid in acetone solution is 0.1 in light of the ranges 3740-3251 and 3740-3345Å. With light of constant intensity, the rate of reaction diminishes as exposure continues. It increases with increasing light intensity, approaching a limit. Kögel assumes that before exposure the normal molecules of the aldehyde are in equilibrium in solution with an intermediate substance, and that it is this substance which reacts photochemically with the normal molecules. This conclusion, which he applies also to *o*-nitrobenzaldehyde, was based upon an observed diminution of the absorption coefficients of the solution with rise in temperature. This was ascribed to the formation of a substance with relatively small absorption coefficients.

Davies⁷² notes that 5-nitro-2-methoxy-3-ethoxybenzaldehyde undergoes no change of color or melting point when exposed in pure acetone solution for 25 hours to ultraviolet rays. On the other hand, another nitration product (melting point 85°C.) of 2-methoxy-3-ethoxysalicylaldehyde obtained by precipitation with water rapidly becomes greenish-blue under the same conditions.

AROMATIC KETONES

Ciamician and Silber⁷³ showed that when an alcoholic solution of benzophenone is exposed to sunlight, the ketone is reduced to benzopinacol and the alcohol is oxidized to aldehyde. Cohen⁷⁴ extended the observations to include a number of substituted ketones and a variety of primary and secondary alcohols. Böeseken, Cohen and Langedijk⁷⁵ gave data on the absorption of benzophenone, fluorenone and terephthalophenone for the region 3600 to 4500Å and pointed out that their maximum absorption did not occur in the wave-length region which was photochemically active.⁷⁶

To throw light on the nature of the primary reaction involved, Böeseken and Visser⁷⁷ determined the photoelectric threshold of benzophenone and found it to lie between 3025 and 2537Å. The absorption band at 2600Å would seem, therefore, to correspond to ionization of the molecule, a process unusually encountered in photochemical processes. No absorption bands were found in the region of excitation, 4070 to 3800Å.

Having shown that a small amount of sodium alcoholate can effect the decomposition of a large amount of benzopinacol into a mixture of benzohydrol and benzophenone, Bachmann⁷⁸ combined this reaction with the photochemical reaction by conducting the latter in solutions containing a small amount of sodium alcoholate. The ketone regenerated in the decomposition of the pinacol into hydrol and ketone goes through the photochemical change again, and the series of reactions is repeated until eventually the hydrol is the sole product. In the case of benzophenone and isopropyl alcohol, the reactions are:

⁷² Davies, W., *J. Chem. Soc.*, **123**, 1590 (1923).

⁷³ Ciamician, G., and Silber, P., *Ber.*, **33**, 2911 (1900).

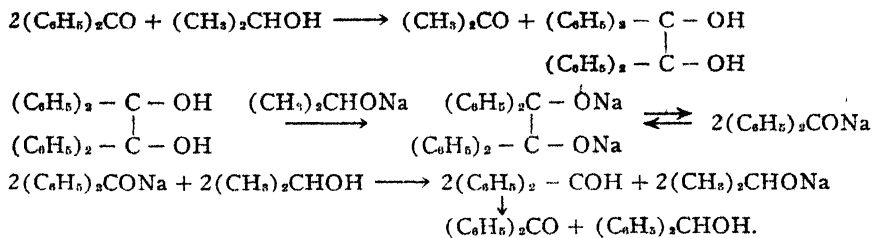
⁷⁴ Cohen, W. D., *Rec. trav. chim.*, **39**, 242 (1920).

⁷⁵ Böeseken, J., Cohen, W. D., and Langedijk, S. L., *Rec. trav. chim.*, **44**, 173 (1925), **46**, 383 (1927).

⁷⁶ For more recent data on the absorption of benzophenone and other ketones, see Tasaki, T., *Acta Phytochim.*, **2**, 49, 199 (1925); **3**, 259 (1927); Anderson, L. C., *J. Am. Chem. Soc.*, **55**, 2094 (1933). Anderson, L. C., and Gooding, C. M., *J. Am. Chem. Soc.*, **57**, 999 (1935); Purvis, J. E., *J. Chem. Soc.*, **127**, 9 (1925). Rupe, H., Collin, A., and Schmiderer, L., *Helv. Chim. Acta*, **14**, 1340 (1931). Rupe, H., Pedrini, F., and Collin, A., *Helv. Chim. Acta*, **15**, 1321 (1932); Rupe, H., Collin, A., and Sigg, W., *Helv. Chim. Acta*, **14**, 1355 (1931); Ley, H., and Wingchen, H., *Ber.*, **67B**, 510 (1934).

⁷⁷ Böeseken, J., and Visser, G. H., *Rec. trav. chim.*, **47**, 1037 (1928); *Chem. Abs.*, **23**, 2660 (1929).

⁷⁸ Bachmann, W. E., *J. Am. Chem. Soc.*, **55**, 355, 391 (1933).



A solution of benzophenone in isopropyl alcohol containing sodium isopropylate becomes greenish-blue on exposure to sunlight, the color being characteristic of the sodium ketyl radical. When the solution is protected from light, the color disappears by the action of the sodium ketyl radical with isopropyl alcohol. Renewed exposure to sunlight restores the color, but when after several days of exposure all of the ketone has been reduced, the solution has again become colorless.

In agreement with the observation of Cohen that Michler's ketone, phenyl- α -naphthyl ketone, fluorenone and 4-phenylbenzophenone are not photochemically reduced to pinacols, Bachmann found that Michler's ketone and phenyl- α -naphthyl ketone could not be reduced to hydrols in this way. Fluorenone underwent a different type of reaction, not photochemical. 4-Phenylbenzophenone, however, was reduced nearly quantitatively to 4-phenylbenzohydrol. In the absence of the alcoholate, it was found to be reduced to the pinacol, 4,4'-diphenylbenzopinacol. Several other substituted ketones behaved in accordance with the new mechanism, yielding hydrols. These included 4-methylbenzophenone, 4,4'-dimethylbenzophenone, 4-methoxybenzophenone, 4-chloro-4'-methoxybenzophenone and 4-chlorobenzophenone. The photochemical reduction process as modified by Bachmann⁷⁹ is suitable for the preparation of benzopinacol.

Migita⁸⁰ finds that di-*p*-methoxybenzophenone in alcohol is reduced in sunlight to the pinacol.

At 100°C., benzophenone itself undergoes no change when irradiated for nine hours by a mercury arc, and acetophenone none after seven hours.⁸¹ When 0.1 molar solutions in hexane or benzene were irradiated, however, benzopinacol crystallized out with a quantum efficiency of 0.04. None was formed when the solvent was carbon tetrachloride.

According to Jenkins,⁸² several ketones of the type $C_6H_5COCH_2C_6H_5$ on standing in light and air undergo autoxidation, yielding acids and aldehydes. Thus $C_6H_5CH_2COC_6H_4Cl-2$ gives benzaldehyde and *o*-chlorobenzoic acid.

Paternò and Chieffi⁸³ observed on exposing benzophenone and phenylacetic acid in benzene to sunlight for five months that benzopinacol and triphenyllactic acid were formed. de Fazi⁸⁴ in repeating these experiments always found pressure due to carbon dioxide, on opening the tubes. The reaction of benzophenone with butyric acid also produces carbon dioxide. In the case of the phenylacetic acid reaction, by opening the tube, removing the crystalline deposit of $\alpha\beta$ -triphenyl- β -hydroxypropionic acid and benzophenone, and restarting the reaction, successive

⁷⁹ Bachmann, W. F., *Organic Syntheses*, New York, John Wiley & Sons, Inc., 14, 8 (1934).

⁸⁰ Migita, M., *Bull. Chem. Soc. Japan*, **7**, 334 (1932); *Chem. Abs.*, **27**, 716 (1933).

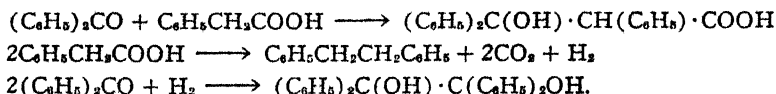
⁸¹ Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934).

⁸² Jenkins, S. S., *J. Am. Chem. Soc.*, **57**, 2733 (1933).

⁸⁸ Paternò, E., and Chieffi, G., *Gazz. chim. ital.*, **40**, II, 321 (1910); *Chem. Abs.*, **5**, 2632 (1911).

⁴ de Fazi, R., *Atti accad. Lincei*, **6**, 266 (1925); *Chem. Abs.*, **20**, 594 (1926); *Gazz. chim. ital.*, **57**, 551 (1927); *Atti II congr. naz. chim. pura applicata*, 1287 (1926); *Chem. Abs.*, **22**, 2154 (1928).

deposits of this mixture could be obtained. The course of the reaction is believed to be:



The ability of benzylphenylacetate to react with benzophenone was believed to account for the fact that only a small amount of this compound could be isolated. Irradiation of a similar mixture of phenylacetic acid, benzophenone and benzene in a quartz tube by a mercury arc for 100 hours gave no triphenyllactic acid and only traces of carbon dioxide. Irradiation with a 2000 C.P. Osram lamp, however, produced abundant quantities of these substances. Exposure of phenylacetic acid alone in benzene to sunlight for six months gave little carbon dioxide and a little of a yellow oil. The Osram lamp gave detectable quantities of carbon dioxide in 24 hours. After 280 hours, there were fairly large quantities of gas and some crystals, probably of *s*-diphenylethane.

4,4'-Tetrachlorodimethylbenzophenone is very sensitive to light and is transformed by it into a plastic mass.⁸⁵ A similar behavior was observed in the case of 4,4'-di(hydroxymethyl)benzophenone. The *N*-alkyloximes of benzophenone also resinify and decompose rapidly in ultraviolet light.⁸⁶ β -*o*-Nitrophenylethylketone loses a molecule of water on irradiation and gives a substance with acidic properties, which melts about 300°C.⁸⁷

After a week in direct sunlight in a sealed glass tube, an alcoholic solution of *o*-benzophenonecarboxylic acid yielded the dilactone of tetraphenyldihydroxyethane-dicarboxylic acid. Similar reactions were given by *p*-tolyl-*o*-benzoic acid and acetophenone-*o*-carboxylic acid.⁸⁸ Straus, Muffat and Heitz⁸⁹ noted a reaction whereby 1-phenylpyrazolines are obtained by the action of phenylhydrazine on certain aromatic ketones, owing to the extraordinary ease with which the hydrazones first formed rearrange.

From an investigation of diketones, Porter, Ramsperger and Steel⁹⁰ find that under the influence of ultraviolet radiation, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200°C. or more. In dilute alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin. In aqueous alcohol in contact with air, it is converted into benzoic acid. Further oxidation of the latter gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in its presence, were never found in the exposed benzil solutions. Marchlewski and Wyrobek⁹¹ find benzil to absorb strongly with a maximum at 2590Å.

⁸⁵ Connerade, E., *Bull. soc. chim. Belg.*, **43**, 447 (1934); *Chem. Abs.*, **29**, 768 (1935); *Bull. soc. chim. Belg.*, **42**, 311 (1933); *Chem. Abs.*, **27**, 507 (1933).

⁸⁶ Martynoff, M., *Ann. chim.*, **7**, 424 (1937); *Chem. Abs.*, **31**, 4973 (1937). For anisalacetophenone, see Stobbe, H., and Hensel, A., *Ber.*, **59**, 2254 (1926).

⁸⁷ Tănăsescu, I., and Tănăsescu, E., *Bull. soc. chim.*, **3**, 865 (1936).

⁸⁸ Limaye, D. B., *J. Univ. Bombay*, **1**, Pt. 2, 52 (1932); *Chem. Abs.*, **27**, 2097 (1933).

⁸⁹ Straus, F., Muffat, C., and Heitz, W., *Ber.*, **51**, 1457 (1918).

⁹⁰ Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, **45**, 1827 (1923).

⁹¹ Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, **93**, 1929A; *Chem. Abs.*, **23**, 5405 (1929).

PHENOLS

The rays of the quartz mercury lamp, according to Gibbs,⁹² color pure phenol light red, in the presence of oxygen, with remarkable rapidity (about one minute). Dermatol (bismuth subgallate) on irradiation produces a violet-colored pigment known as galloflavin.⁹³ Exposure of 3,4-chloronitrosophenol in ethyl alcohol⁹⁴ transforms it into resinous products.

The *m*-cresols are said to color more rapidly on exposure to light and air than the *o*- and *p*-cresols, and gentisic acid and its esters are even more readily colored.⁹⁵ Viktorin⁹⁷ finds the oxidation of phloroglucinol by atmospheric oxygen to evolve ultraviolet radiations.⁹⁸ Schweckendiek⁹⁹ finds guaiacetic acid, like guaiaretic acid, to be sensitive to light, the sensitivity being increased by the addition of collodion, Zapon lacquer, or a solution of sulfur in carbon disulfide. The product is green and results from an oxidation process. It may be employed as a photographic process, the green image being fixed with a mixture of ammonium acetate and benzene.

Aside from these scattered observations, little definite seems to be known regarding the photochemistry of the phenols. There is, however, much data on their absorption spectra. Indeed, by measurements in solutions containing various amounts of added alkali, it is possible to determine the dissociation constant of phenol by the changes in its absorption spectrum.¹⁰⁰

QUINONES

Because of their importance for theories of color, the visible and ultraviolet absorption spectra of the quinones, especially benzoquinone, have been much investigated. This topic, however, lies beyond the scope of this work. Benzoquinone as vapor exhibits a region of fine band absorption from 4800 to 4200Å, one of narrow bands between 3100 and 2600Å, and a continuous region at shorter wavelengths.¹⁰¹

⁹² Gibbs, H. D., *J. Am. Chem. Soc.*, **34**, 1193 (1912).

⁹³ Guyot, R., *Bull. soc. pharm. Bordeaux*, **66**, 18 (1928); *Chem. Abs.*, **23**, 4015 (1929).

⁹⁴ Hodgson, H., and Kershaw, A., *J. Chem. Soc.*, 1553 (1929). Some data on the effects of various wave-lengths on the oxidation of *d*-catechin in the presence of a complex cobalt salt have been recorded by Shibata and Goda.⁹⁶

⁹⁵ Shibata and Goda, *Iwata Inst. Plant Biochem., Publ.*, **2**, 175 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936).

⁹⁶ Gibbs, H. D., Williams, R. R., and Pratt, D. S., *Philippine J. Sci.*, **7**, 79 (1912).

⁹⁷ Viktorin, O., *Chem. Listy*, **29**, 245 (1935); *Brit. Chem. Abs.*, **A**, 7 (1936).

⁹⁸ In a method of making photographic prints, the sensitive layer may contain a colorless inorganic oxidizing agent such as nitric acid or lithium nitrate, and a cyclic organic amino-compound such as aminophenol, benzidine, dianisidine, etc. These compounds are sensitive only to ultraviolet light which produces colored compounds. After exposure, the unexposed portions may be washed out with water or other solvent, the colored product being insoluble. British P. 413,093, April 20, 1933, to N. V. Philips' Gloeilampenfabriken. *Brit. Chem. Abs.*, **1934B**, 813.

⁹⁹ Schweckendiek, C., *Diss.*, Giesen, 1927; *Brit. Chem. Abs.*, **A**, 1041 (1927).

¹⁰⁰ Stenstrom, M., and Goldsmith, N., *J. Phys. Chem.*, **30**, 1683 (1926); Stenstrom, M., and Reinhard, M., *J. Phys. Chem.*, **29**, 1477 (1925); Job, P., *Compt. rend.*, **186**, 1546 (1928). For other data on the absorption of phenols, see Kepianka, E., and Marchlewski, L., *Bull. soc. chim.*, **35**, 1613 (1924); Valyashko, N. A., *J. Russ. Phys.-Chem. Soc.*, **58**, 779 (1926); *Chem. Abs.*, **22**, 949 (1928); Purvis, J. E., *Proc. Cambridge Phil. Soc.*, **23**, I, 588 (1927); Conrad-Billroth, H., *Z. physik. Chem.*, **20B**, 222, 227 (1933); Savard, J., *Ann. Chim.*, **9**, 287 (1929); **11**, 287 (1929); *Compt. rend.*, **188**, 782 (1929); Lambrechts, A., *Compt. rend.*, **198**, 1852 (1934); Kepianka, E., and Marchlewski, L., *Bull. intern. acad. Polonaise*, **75**, 1926A; *Bull. soc. chim.*, **39**, 1368 (1926); Goslawski, W., and Marchlewski, L., *Bull. Intern. Acad. Polonaise*, **383** 1931A; de Boer, J. H., and Custers, J. F. H., *Z. physik. Chem.*, **25B**, 238 (1934); Eisenbrand, I., and von Halban, H., *Z. physik. Chem.*, **146**, 30, 101, 111 (1930); Saint-Maxen, A., and Dureuil, E., *Compt. rend.*, **197**, 1411 (1933); Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, **93** 1929A.

¹⁰¹ Lifschitz, I., and Rosenbohm, E., *Z. Physik*, **38**, 61 (1926); Light, L., *Z. physik. Chem.*, **122**, 414 (1926).

Benzoquinone in light effects the oxidation of various alcohols. Leighton and Forbes¹⁰² found that when water was also present in large amounts, the reaction exhibited an induction period during which a dimer of the quinone was believed to be formed. When the solvent was 50-per cent alcohol, there was no inhibition. With wave-lengths shorter than 4350Å, they found the quantum yield to be 0.5 in alcohol and in aqueous alcoholic solutions. It was independent of the wave-length, and in aqueous alcoholic solutions, also of the concentrations. With longer wave-lengths the quantum yields decreased, indicating the existence of a threshold inside the first absorption band. As the concentration of alcohol was decreased, the threshold was displaced toward shorter wave-lengths. These investigators suggested that every absorbed quantum might produce activation, the observed quantum yields being lowered by a secondary reaction which has an efficiency of but 50 per cent. Recently, these results have been challenged by Berthoud and Porret¹⁰³ who observed quantum yields of unity at 4050, 4080 and 4360Å. They found the rates to be independent of the quinone concentration and temperature. The rates decrease slowly with decreasing alcohol concentration, and are proportional to the light intensity. Similar results were obtained with isopropyl alcohol.

The oxidation of ferrous sulfate by benzoquinone, but not the reverse process, is sensitive to light. It proceeds with a quantum yield of unity at 4050, 4080 and 4360Å and is independent of the temperature and concentrations of reactants.¹⁰⁴

AROMATIC ACIDS AND THEIR DERIVATIVES

Benzoic Acid. Kailan¹⁰⁵ found ultraviolet irradiation of aqueous solutions of benzoic acid to yield reducing substances, formic acid and oxalic acid. The velocity of the formation of these substances increased as the square of the concentration. Alcoholic solutions are esterified¹⁰⁶ to the extent of 30 per cent in eight days. The rate is promoted by the presence of a trace of hydrochloric acid.

On exposure to acid and sunlight, the esters of the three hydroxybenzoic acids color more rapidly than the free acids; the *meta* compounds are the most rapidly changed; the *para* compounds are practically unaffected.¹⁰⁷

Decomposition of acetylbenzoyl peroxide by ultraviolet light yields carbon dioxide, toluene, methyl benzoate, methane, phenyl benzoate and complex materials of acid and neutral character.¹⁰⁸ Possibly hydrolysis occurs, the necessary water being liberated in the formation of the complex materials.



Fichter and Schnider¹⁰⁹ found the decomposition of dibenzoyl peroxide in ultraviolet light to yield about 80 per cent of the theoretical quantity of carbon dioxide and diphenyl. The residue, an amorphous resin, was not characterized.

Absorption of potassium cyanide by benzaldehyde in the benzoin condensation is unaffected by irradiation.¹¹⁰ Benzoin, however, is converted into a viscous resin by irradiation, the process being favored by an increase in temperature.

¹⁰² Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **51**, 3549 (1929); for the actinometric use of benzoquinone, see Chapter 7.

¹⁰³ Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 694 (1934).

¹⁰⁴ Porret, D., *Helv. Chim. Acta*, **17**, 703 (1934).

¹⁰⁵ Kailan, A., *Z. physik. Chem.*, **95**, 215 (1920); *J. Chem. Soc.*, **118**, 11, 576 (1920).

¹⁰⁶ Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).

¹⁰⁷ Gibbs, H. D., Williams, R. R., and Pratt, D. S., *Philippine J. Sci.*, **7**, 79 (1912).

¹⁰⁸ Fichter, F., and Willi, E., *Helv. Chim. Acta*, **17**, 1173 (1934).

¹⁰⁹ Fichter, F., and Schnider, A., *Helv. Chim. Acta*, **13**, 1428 (1930).

¹¹⁰ Bousset, R., *Bull. soc. chim.*, **2**, 309 (1935).

Salicylic Acid. Little is known of the photochemical behavior of this acid. Light (but not ultraviolet light) is said to darken the pharmaceutical solutions of sodium salicylate containing sodium bicarbonate. This probably consists in an oxidation with the formation of quinones.¹¹¹ Methyl salicylate becomes colored on exposure to air and sunlight, the tint varying from light yellow for short exposures to reddish-brown for protracted ones.¹¹²

It has been proposed to use such aryl azides as azido-salicylic acid (prepared by the action of sodium azide on diazosalicylic acid) in photographic processes. A layer of the material incorporated in gelatin and exposed under a negative forms a dye, after which the unchanged azide may be washed out.¹¹³

Of 22 anils known to be phototropic, 15 were said to be derivatives of salicylaldehyde. Recently Brewster and Millam¹¹⁴ have added three, one a derivative of salicylaldehyde and the other two of 5-bromosalicylaldehyde.

Mandelic Acid. This acid can be oxidized by methylene blue by wavelengths in the range 2540 to 4360A if uranyl nitrate is employed as photosensitizer. In the mechanism suggested by Ghosh, Narayanamurthi and Roy,¹¹⁵ excited UO_2^{++} ions yield their energy to mandelic acid, which is decomposed with the production of benzaldehyde, carbon dioxide, water and the UO^{+} ion. The latter takes an oxygen atom from water, the hydrogen of which reduces methylene blue to the leuco-compound. Oxygen restores the methylene blue, and light excites the uranyl ion so that the processes may be repeated.

Phthalates. When lead phthalate is exposed in a small quartz crucible to ultraviolet rays, the outer layer decomposes rapidly with the formation of a yellowish-brown substance of unknown composition, but probably containing lead oxide. Under the same conditions mercury phthalate is unaffected.¹¹⁶

Jaeger¹¹⁷ claims the decarboxylation of polycarboxylic acids, for example, the conversion of phthalic into benzoic, by subjecting them at 300° to 420°C. in the presence of reducing gases (hydrogen or water gas) to various types of electrical discharge, ultraviolet light, cathode rays or x-rays.

For refining liquid alkyl esters derived from acids produced by the catalytic oxidation of aromatic hydrocarbons, such as dibutyl phthalate, so that distillation of the ester is rendered unnecessary, and its color improved, the material may be exposed to the action of ultraviolet light.¹¹⁸

An alcoholic solution of 2,4-dihydroisophthalic acid, which appears to react as a quinone derivative, forms acetaldehyde in sunlight.¹¹⁹

Although terephthaldehyde is very stable in the solid state and in solution in benzene in darkness, Suida¹²⁰ finds that its solution undergoes rapid atmospheric oxidation when irradiated by a mercury lamp, a white crystalline deposit being formed. This consists of terephthaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid. The solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution.

¹¹¹ Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **17**, 1203 (1928); Liberalli, C. H., *Bol. assoc. brasil farm.*, **16**, 154 (1935); *Chem. Abs.*, **29**, 5989 (1935).

¹¹² Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).

¹¹³ British P. 333,820, Nov. 3, 1928, to Kalle and Co. *Brit. Chem. Abs.*, **1930B**, 1092.

¹¹⁴ Brewster, C. M., and Millam, L. H., *J. Am. Chem. Soc.*, **55**, 763 (1933).

¹¹⁵ Ghosh, J. C., Narayanamurthi, D. S., and Roy, N. K., *Z. physik. Chem.*, **29B**, 236 (1935).

¹¹⁶ Ekeley, J. B., and Banta, C., *J. Am. Chem. Soc.*, **39**, 762 (1917).

¹¹⁷ Jaeger, A. O., U. S. P. 1,909,357, May 16, 1933, to Selden Co.; *Brit. Chem. Abs.*, **1934B**, 87.

¹¹⁸ Smith, F. D., U. S. P. 1,948,281, Feb. 20, 1934 (to Monsanto Chemical Co.); *Chem. Abs.*, **28**, 2725 (1934).

¹¹⁹ Marzin, A., *J. prakt. Chem.*, **138**, 107 (1933); *Chem. Abs.*, **27**, 5317 (1933).

¹²⁰ Suida, H., *Monatsh.*, **33**, 1173 (1912); *J. Chem. Soc.*, **104** (i), 52 (1913).

The oxidation is not accelerated by the presence of nitrobenzene, which, indeed, exerts a hindering effect. A comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the *para* position. Spectrographic examination indicates that the effective rays are those of wave-lengths between 4000 and 3000Å, but yellow and red light can cause the oxidation to occur, although only very feebly.

Cinnamic Aldehyde and Cinnamic Acid. These compounds exhibit interesting photochemical reactions because, in addition to the features common to the aldehydes and acids, the presence of a double bond in the side chain offers new possibilities of polymerization and stereoisomerization. Cinnamic acid, in alcoholic solution, exhibits one broad absorption band with a maximum at 2710Å. Hydrocinnamic acid, however, in aqueous solution, shows two bands with maxima at 2670 and 2580Å.¹²¹

In sunlight, cinnamic aldehyde reacts with quinone as do other aldehydes. Bargellini and Monti¹²² exposed 10.8 gm. of quinone and 13.2 gm. of cinnamic aldehyde in 100 cc. of benzene in a sealed tube for one month. The quinone was reduced to hydroquinone and the aldehyde oxidized to cinnamic acid. These two products then combined, the reaction being analogous to that between phenanthrene-quinone and certain aldehydes described by Klinger.¹²³ According to Stoermer and Ladewig,¹²⁴ in the presence of a trace of hydrochloric acid, cinnamic acid reacts with alcohol when irradiated, as much as 37 per cent being esterified in eight days.

When thin layers of finely powdered *o*-nitrocinnamic acid are exposed to sunlight, a red substance melting at 120°C. is produced. It is probably hydroxyisatogenic acid, $C_6H_4 \begin{matrix} \text{CH} \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{NO} \end{matrix} \text{C} \cdot \text{COOH}$. This is another¹²⁵ example of a type of reaction frequently encountered.

The presence of a double bond in the side chain of cinnamic acid permits the existence of *cis* and *trans* forms. Photochemical changes may consist of either a stereoisomerism or a polymerization of either form to a dimer. This, together with the fact that *allo*-(*cis*)-cinnamic acid^{125a} is trimorphous, having forms melting at 42°, 58° and 68°C., makes the photochemistry of this compound an intricate subject which has been much investigated, with confusing results. Since the matter is rather highly specialized, space does not permit a complete discussion.¹²⁶

Stoermer¹²⁷ showed that ultraviolet light changes the less fusible stable to the more reactive labile forms. The extent of the transformation was thought to be dependent upon the energy differences between the stereoisomers. Many derivatives of cinnamic acid were studied¹²⁸ and it was believed that in most cases an

¹²¹ Marchlewski, L., and Wyrobek, O., *Bull. acad. Polonaise*, 331 (1929); *Chem. Abs.*, 24, 3711 (1930). Ley, H., and Dreinhöfer, R., *Z. wiss. Phot.*, 29, 134 (1930); Ramart-Lucas and Trivédi, R., *Compt. rend.*, 195, 783 (1932); Purvis, J. E., *J. Chem. Soc.*, 780 (1927).

¹²² Bargellini, G., and Monti, L., *Gazz. chim. ital.*, 60, 474 (1930); *Chem. Abs.*, 25, 96 (1931).

¹²³ Klinger, H., *Annalen*, 249, 137 (1888); 382, 211 (1911); *Ber.*, 24, 1340 (1891); 31, 1214 (1898). In most of this work many of the quinone reactions followed a different course.

¹²⁴ Stoermer, R., and Ladewig, H., *Ber.*, 47, 1803 (1914).

¹²⁵ Tănăsescu, I., *Bull. soc. chim.*, 41, 1074 (1927).

^{125a} The ordinary *trans*-cinnamic acid melts at 133°C.

¹²⁶ de Jong, A. W. K., *Chem. Weekblad*, 26, 270 (1929) has compiled a large number of references regarding the effects of sunlight on the *cis*- and *trans*-cinnamic acids.

¹²⁷ Stoermer, R., *Ber.*, 42, 4865 (1909); *J. Chem. Soc.*, 8 (ii), 114 (1910).

¹²⁸ Stoermer, R., with Frederici, Brautigam and Neckel, *Ber.*, 44, 637 (1911).

equilibrium was attained. The number after each of the following compounds represents the percentage of the less fusible form which, at equilibrium, has been transformed: methyl-*o*-nitro-*o*-methoxycinnamate, 80; *p*-methoxycinnamic acid, 25; sodium-*o*-chlorocinnamate, 10; *o*-anisylcinnamic acid, 35-40; *o*-anisylcinnamide, 70; *o*-anisylcinnam-methylamide, 36; and the corresponding ethylamide, 40; β -*o*-anisyl- α -methylcinnamic acid, 5, and the corresponding amide, 5; the form of cinnamic acid melting at 42°C., 30-40. In the case of *o*-chlorocinnamic acid, when glacial acetic acid was employed as solvent, it was observed that, in addition to the expected isomerization, part of the acid combined with the solvent.

When daylight or sunlight, rather than the light of the mercury arc is used, polymerization reactions also occur with the formation of dimers¹²⁹ although isomerization occurs with either sunlight or mercury arc light. Fused *cis*-cinnamic acid is transformed extensively to the *trans* form after 96 hours of mercury arc irradiation. Similarly, α -*trans*-cinnamic acid, fused or in solution, isomerized to the equilibrium mixture. For this change, radiations of wave-length 3200 to 2700Å are most effective. The reaction is greatly accelerated by the addition of hydrochloric acid.

When the solid acids or their aqueous suspensions are exposed to sunlight, this change is accompanied by polymerization; α -*trans*-cinnamic acid yields mainly the dimer α -truxillic acid with a little β -truxinic acid. *Allo*-cinnamic acid (*cis*) yields as its polymerization product chiefly β -truxinic acid, together with the isomerization product *trans*-cinnamic acid and its dimer, a little α -truxillic acid. The latter change took place to the extent of 71 per cent after 196 hours in sunlight, but after 200 hours of the mercury arc irradiation only to the extent of 4.4 per cent. Very similar results were recorded for the polymerization of the *trans* acid. Long ultraviolet rays accordingly favor polymerization, but the shorter ones hinder it and exert a depolymerizing action on truxinic and truxillic acids. Each dimer when irradiated by the shorter radiations depolymerizes to the monomer from which it is originally formed by the longer rays.

The metastable β -form of *trans*-cinnamic acid is much more readily isomerized than the stable α -*trans*-cinnamic acid which therefore yields on polymerization but little β -truxinic acid and much α -truxillic acid.

Experiments of this type are further complicated by the fact that some autooxidation to benzaldehyde and in some cases to benzoic acid also occurs. On long illumination of *trans*-cinnamic acid the yield of the dimer, α -truxillic acid, decreases and that of benzaldehyde increases. Analogous results are obtained in the irradiation of *cis*-cinnamic acid.

Stobbe and Zschoch¹³⁰ found that the monomeric *trans*-cinnamic acid in 0.0001*N* alcoholic solution absorbs light strongly, although its saturated dimer, α -truxillic acid, is almost completely transparent and begins to absorb only in a 40-mm. layer of a 0.001*N* solution. In a 10-mm. layer of 0.01*N* solutions, its end absorption begins at a wave-length about 600Å units shorter than that of the monomer. This difference in absorption accounts for the differing effects of longer and shorter ultraviolet radiations on polymerization and depolymerization. These compounds do not fluoresce.

The quantum yields for the isomerization by the 3130Å line have been found to

¹²⁹ Stobbe, H., *Ber.*, **52B**, 666 (1919); Stobbe, H., and Steinberger, F. K., *Ber.*, **55B**, 2225 (1922). See also de Jong, A. W. K., *Chem. Abs.*, **16**, 2683 (1922); **6**, 2746 (1912); Stoermer, R., and Scholtz, F., *Chem. Abs.*, **15**, 1888 (1921) and Stobbe, H., and Lehfeldt, A., *Ber.*, **58B**, 2415 (1925).

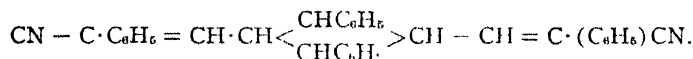
¹³⁰ Stobbe, H., and Zschoch, F., *Ber.*, **60B**, 457 (1927).

be as follows: Cinnamic acid, 0.003 molar, 0.61; 0.002 molar, 0.53; isocinnamic acid, 0.003 molar, 0.21; 0.002 molar, 0.15.¹³¹

Various derivatives of cinnamic acid are subject to similar transformations. Stobbe¹³² observed methyl *trans*-cinnamate to be converted to a small extent by six months of exposure to sunlight into methyl α -truxillate (2.9 per cent) derived from the solid ester and 0.2 per cent of Liebermann's polyester formed from portions which had been melted by the heat of the sun. The remainder was unchanged. *trans*-Cinnamide was in five months converted into α -truxillidamide to the extent of 75 per cent. *trans*-Cinnamanilide remains unchanged after six months' exposure in the solid state or suspended in hydrochloric acid. *allo*-Cinnamic anhydride is converted into a mixture of 80 per cent *trans*- and 20 per cent *allo*-anhydride without the production of β -truxinic anhydride, but *trans*-cinnamic anhydride remains unchanged, aside from slight resin formation. Cinnamaldehyde, after eight months in sunlight, yields a mixture of 60 per cent unchanged aldehyde, 33 per cent cinnamic acid and 7 per cent polycinnamaldehyde, apparently a tetramer, which does not yield an oxime or react with ammoniacal silver nitrate or Schiff's reagent. At least 91 per cent of α -bromocinnamic acid remains unchanged after seven months in sunlight or 375 hours in the light of a mercury vapor lamp; the remainder is converted by autooxidation into oxalic acid, benzoic acid and free bromine. No polymerization or resin formation occurred. Gulland and Virden¹³³ find the yellow *trans*-2-amino acid obtained by the reduction of 3,4,2',5'-tetramethoxy-2-nitro-*trans*- α -phenylcinnamic acid, in alcoholic solution to give after several days in ultraviolet light, 7,8,2',5'-tetramethoxy-3-phenylcarbostyryl. The action of ultraviolet light on the sodium salt of *trans*-2-nitro-3,4,2',5'-tetramethoxy- α -phenylcinnamic acid gives a small yield of the *cis* form.

o-Hydroxycinnamic acid is oxidized by peracetic acid in darkness to *cis-cis*-muconic acid in very small amount; in light a more or less complete isomerization to the *trans-trans* acid occurs.¹³⁴ *cis-cis*-Muconic acid, in 96 per cent alcohol with a trace of iodine, is almost quantitatively rearranged into the *trans-trans* compound.

Acids containing the cinnamylidene residue and their nitriles have also been extensively investigated. Solutions of α -phenylcinnamylidenecetonitrile in benzene or chloroform in either the presence or absence of iodine in sunlight form two dimers, one melting at 197°C. and the other at 215°C.¹³⁵ The former is 1,3-diphenylcyclobutane-2,4-diatropo-nitrile, also called 1,3-diphenyl-2,4-*bis*-(β -phenyl- β -cyanovinyl)cyclobutane:



The isomerism of the two dimers may be of the *cis-trans* type, depending on a difference of location of the phenyl and cyano- groups at one or both of the double bonds of the side chain, since on treatment with permanganate both yield α -truxillic acid.

According to Lohaus,¹³⁶ exposure of a solution of the stable ethyl cinnamylidenecyanoacetate in ethyl alcohol in the presence of a little sulfuric acid gives after one day in sunlight a labile form. Further exposure of the crystalline material recovered yields a cyclobutane derivative previously described by Reimer (1911, 1913). In the absence of sulfuric acid, however, the original compound polymerizes to an open-chain dimer, melting at 165°C. The labile form of ethyl cinnamylidene cyanoacetate is rapidly converted into its stable form when its alcoholic solution, containing iodine, is exposed to sunlight in quartz vessels.

allo-(*trans,cis*)-Cinnamylidenecetic acid is converted into the normal (*trans-trans*) form by irradiation of its solutions in the presence of iodine.¹³⁷ Equilibrium is attained when 90 per cent conversion has been effected, this equilibrium being independent of the concentration of iodine and the intensity of the light and but little dependent on the temperature. Constant unimolecular rate constants could be obtained when concentrations of iodine greater than 0.024*N* were used, but at lower concentrations the rate

¹³¹ Vaidya, B. M., *Proc. Roy. Soc.*, **A129**, 299 (1930).

¹³² Stobbe, H., *Ber.*, **58B**, 2859 (1925); *Chem. Abs.*, **20**, 1612 (1926).

¹³³ Gulland, J. M., and Virden, C. J., *J. Chem. Soc.*, 1478 (1928).

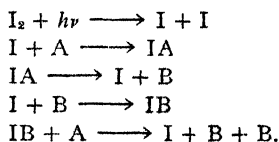
¹³⁴ Grundmann, C., and Trischmann, H., *Ber.*, **B69**, 1755 (1936); *Chem. Abs.*, **30**, 6354 (1936).

¹³⁵ Stobbe, H., and Kuhrmann, F., *Ber.*, **58B**, 85 (1925); *J. Chem. Soc.*, **128**, I, 253 (1925).

¹³⁶ Lohaus, H., *Annalen*, **514**, 137 (1934); *Chem. Abs.*, **29**, 1796 (1935).

¹³⁷ Ghosh, J. C., and Mitra, M. N., *J. Indian Chem. Soc.*, **3**, 273 (1926); *Brit. Chem. Abs.*, **1927A**, 560.

constant for the forward reaction showed a gradual increase with time indicative of an induction period. This was observed only when freshly prepared solutions were used. With increasing iodine concentrations the rate constant passed through a maximum. The values of the constants decreased with increasing initial concentrations of the compound. They were proportional to the intensity of the light (5000Å). A quantum yield of 423 was found. Green light was most effective, then blue, yellow and red light.¹³⁸ The rates were highest in methanol, and decreased in other solvents in the order ethanol, mixtures of ethanol and water, and mixtures of chloroform and methanol. In chloroform the rates were very low in comparison with those in solutions containing the hydroxyl group. For benzene or chloroform as solvents Ghosh, Murthi and Das-Gupta¹³⁹ have suggested the following reactions as entering the mechanism, in which A represents the *allo*-acid employed and B the normal acid formed.



They also find that the rate constant increases with the light intensity, at first rapidly and then more slowly; it also varies with the square root of the energy absorbed.

Vorländer and Gieseler¹⁴⁰ find that exposure of a solution of the sodium salt of *trans-trans-p*-methoxycinnamylideneacetic acid to ultraviolet light causes the formation of salts of two acids (or mixtures of acids), melting at 90-96° and 106-110°C., respectively. Both of these regenerate the original acid when their benzene solutions with iodine are exposed to sunlight. Under these conditions, *allo-p*-methoxycinnamylideneacetic acid is converted into the *trans-trans* form. Cinnamylidene-*m*-nitroacetophenone yields, in 10-per cent chloroform solution after 15 days in sunlight or 12 hours in ultraviolet from a mercury lamp, a semisolid substance which slowly forms a resin with a fracture like that of colophony.¹⁴¹ In this resinification, it differs from cinnamylideneacetophenone, which polymerizes under the action of light.¹⁴²

The ability of dicinnamalacetone to form insoluble, noncrystalline products on exposure to light when exposed in a laver with shellac and a basic dye has led Seymour¹⁴³ to propose its use in photographically printing dyed relief images.¹⁴⁴

The photochemical addition of bromine to α phenylcinnamonitrile¹⁴⁵ under conditions of slight absorption of light proceeds at a rate proportional to the square root of the intensity and to the 1.5 power of the bromine concentration. Under conditions of total absorption, it is proportional to the square root of the intensity and to the bromine concentration. The temperature coefficient is 1.4. The dibromide, once formed, can also be photochemically decomposed in the presence of bromine, which acts as a sensitizer. The rate is retarded by the presence of a large excess of the nitrile.

Halogenation of Cinnamic Acid. The rate of photobromination of cinnamic acid is dependent upon the form of the acid employed. The thermal rate for *allo*-cinnamic acid, melting at 68°C., is increased five-fold by yellow light, but that of the ordinary acid (melting 133°C.) is increased forty-fold.¹⁴⁶ In darkness, the

¹³⁸ Ghosh, J. C., Das Gupta, D. N., Roy, N. C., and Chatterjee, H. K., *J. Phys. Chem.*, **34**, 2771 (1930).

¹³⁹ Ghosh, J. C., Murthi, D. S. N., and Das Gupta, D. N., *Z. physik. Chem.*, **B26**, 255, 267 (1934).

¹⁴⁰ Vorländer, D., and Gieseler, K., *J. prakt. Chem.*, **121**, 247 (1929); *Chem. Abs.*, **23**, 3912 (1929).

¹⁴¹ Giua, M., *Gazz. chim. ital.*, **55**, 567 (1925); *Chem. Abs.*, **20**, 749 (1926).

¹⁴² Stobbe, H., and Rücker, C., *Ber.*, **44**, 869 (1911); *Chem. Abs.*, **5**, 2253 (1911).

¹⁴³ Seymour, M. W., U. S. P. 2,063,348, Dec. 8, 1936, to Eastman Kodak Co.; *Chem. Abs.*, **31**, 621 (1937).

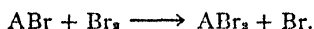
¹⁴⁴ For a study of the photodimers of cinnamalmalonic acid, see Stobbe, H., Hensel, A., and Simon, W., *J. prakt. Chem.*, **110**, 129 (1925).

¹⁴⁵ Berthoud, A., and Nicolet, G., *Helv. Chim. Acta*, **10**, 417 (1927); *J. chim. phys.*, **25**, 40 (1928).

¹⁴⁶ Meyer, J., and Pukall, W., *Z. physik. Chem.*, **A145**, 360 (1929); see also Padoa, M., and Vita, N., *Gazz. chim. ital.*, **58**, 3 (1928).

rate of bromination of the *allo*-acid melting at 58°C. is greater than that of the form melting at 68°, but the form melting at 42°C. is more rapidly brominated than either of these. These differences led Meyer and Pukall to regard the three forms of the *allo*-acid as isomers, unexplained by ordinary stereochemical concepts, rather than as polymorphs. They were unable to obtain constant rate values by the use of yellow, blue or yellowish white light and the 133°C. ordinary cinnamic acid, but with red or green light found the reaction to be bimolecular.

Yajnik and Uppal¹⁴⁷ found that, for equimolar concentrations of bromine and cinnamic acid in either carbon disulfide, carbon tetrachloride or chloroform, the formula for unimolecular reactions gave sufficiently constant values for the rate constant. A temperature coefficient of 2.8, increasing with the wave-length used, was observed by Ghosh and Purkayastha,¹⁴⁸ who found the velocity coefficient independent of the concentration of bromine. It increased with the initial concentration of the cinnamic acid and varied as the square root of the intensity of incident blue light. For green light, the increase was greater. They found that there was an induction period and an after-effect, from which they assumed the existence of a complex intermediate. Excited bromine molecules were considered to function in the mechanism. One quantum of light was observed to form 426 molecules of dibromophenylpropionic acid in one experiment. Other values were, in carbon tetrachloride, 22 at 5330 Å and 43 at 4880 Å, and in carbon disulfide, 101 and 156, respectively. Berthoud and Béranek¹⁴⁹ believed the velocity in carbon tetrachloride to be affected by an unknown catalyst, the effect of which they could not completely eliminate. They differed from the Indian workers in finding the reaction independent of the concentration of acceptors, such as cinnamic acid. With strong absorption, it was nearly first order with respect to bromine, but with weak absorption, it was of 3/2 order. The quantum yield was about 36 with a violet filter and 10 with a green filter. Rotating sectors, transmitting 50 and 25 per cent of the light, reduced the velocity to 65 and 43 per cent. This use of sectors has been criticized by the Indian workers. The mechanism of Berthoud assumes that bromine atoms participate in reaction chains.



Ghosh, Bhattacharya and Murthi¹⁵⁰ find the combined effect of any two radiations selected from 546, 436 and 406 mμ to be less than the sum of the two separate effects.

Bauer and Daniels¹⁵¹ confirmed the chain nature of the reaction but found much lower quantum yields, 1 to 15 or more, varying with the concentration of the bromine and the temperature. The yields decrease linearly with dilution to unity at infinite dilution. The nature of the reaction was thought to be complex since, in addition to the primary process with a quantum yield of unity, it involved also a photo-excited thermal reaction which can be suppressed by the use of low

¹⁴⁷ Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem. Abs.*, **1930A**, 174. See also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, **2**, 243 (1928) and Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

¹⁴⁸ Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926); *Quart. J. Indian Chem. Soc.*, **4**, 409, 553 (1927); *Brit. Chem. Abs.*, **1928A**, 172, 256.

¹⁴⁹ Berthoud A., and Béranek, J., *J. chim. phys.*, **24**, 213 (1927); *Helv. Chim. Acta*, **10**, 289 (1927).

¹⁵⁰ Ghosh, J. C., Bhattacharya, S. K., and Murthi, M. L. N., *J. Indian Chem. Soc.*, **14**, 482 (1937); *Chem. Abs.*, **32**, 4881 (1938).

¹⁵¹ Bauer, W. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 378 (1934); **56**, 2014, 2564 (1934); see also Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 235 (1933), and Ogg, R. A., Jr., *J. Am. Chem. Soc.*, **58**, 607 (1936).

bromine concentrations and low temperatures. They believed that this reaction forms an example of an energy chain carried by activated bromine molecules.

In ether in diffuse sunlight at -10° , cinnamic aldehyde adds the theoretical amount of bromine, but in brighter light, substitution also occurs. *trans*-Cinnamic acid in sunlight added practically the theoretical amount.¹⁵² *m*-Methoxycinnamic acid in boiling carbon tetrachloride gave α,β -dibromo- β , 3-methoxyphenylpropionic acid. In darkness in acetic acid, there is a quantitative yield of the 6-bromo-derivative of the cinnamic acid and this is also formed in boiling acetic acid in sunlight. In boiling chloroform, a mixture of the two products forms. Analogous results are found with the ethyl ester in these solvents. 6-Bromo-derivatives of the methoxycinnamic acid, on bromination in carbon tetrachloride in sunlight give the β -6-bromo-derivative of the propionic acid. α -Bromo-*m*-methoxy-*allo*-cinnamic acid is transformed into α -bromo-*m*-methoxycinnamic acid (the *trans* form) by sunlight.

For the chlorination of cinnamic acid, Basu¹⁵³ found, in carbon tetrachloride exposed to the full radiation from a quartz lamp, at 22.6°C ., a unimolecular rate constant of 3.8×10^{-3} , with respect to chlorine. It was unaffected by changes in the cinnamic acid concentrations. In darkness, there was a constant of 4×10^{-5} . At the wave-lengths 3665, 4040 and 4360\AA , the quantum yields were 7, 4, and 2. Since no fluorescence could be observed, Basu proposed a mechanism involving, of the chlorine atoms produced in the primary process, only the excited ones as carriers of the chains. The chain length was thought to depend upon the amount of energy associated with the intermediary monochloride of cinnamic acid. Berthoud and Porret¹⁵⁴ believed this reaction to follow the same laws as the photobromination. The life of a reaction chain was considered to be less than 0.02 second. The quantum yields varied with the experimental conditions, being 2.4 in one case. The rate was independent of the concentration of acid, and proportional to the chlorine concentration for total absorption, or to the two-thirds power for weak absorption. It was also proportional to the square root of the light intensity.

Woods and Poulter¹⁵⁵ believed they had demonstrated the ability of ultraviolet light to alter slightly the polarity of the double bond in cinnamic acid. When its solution in absolute ether was irradiated for an hour with the highly polar reagent hydrogen bromide, the residue after evaporation of the ether yielded to ligroin a small portion of material which on recovery from the solvent melted at about 50°C . and had physical properties very similar to those of the compound $\text{C}_6\text{H}_5\text{CH}_2\text{-CHBrCOOH}$.¹⁵⁶

Coumarin, the inner lactone of *o*-hydroxycinnamic acid, also possesses a double bond and is subject to reactions analogous to those of cinnamic acid. It exhibits two absorption maxima at 3200 and 3600\AA ¹⁵⁷ but when one or two hydroxyl groups are introduced into the benzene ring, the resulting products show only one absorption maximum. It has been found that when certain immature plants, which when mature contain coumarin, are irradiated by a mercury-vapor lamp, the odor of coumarin becomes perceptible in a few minutes.¹⁵⁸

¹⁵² Duquenois, P., *Bull. soc. chim.*, **4**, 193 (1937).

¹⁵³ Basu, K. P., *J. Indian Chem. Soc.*, **6**, 341 (1929); *Chem. Abs.*, **24**, 784 (1930)

¹⁵⁴ Berthoud, A. and Porret, D., *Helv. Chim. Acta*, **17**, 237 (1934).

¹⁵⁵ Woods, G. M., and Poulter, T. C., *Proc. Iowa Acad. Sci.*, **35**, 217 (1928); *Chem. Abs.*, **24**, 1101 (1930).

¹⁵⁶ For data on the photobromination of α -phenylcinnamic acid, see Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 1548 (1934).

¹⁵⁷ Tasaki, T., *Acta. Phytochim.*, **3**, 21 (1927); *Chem. Abs.*, **22**, 1543 (1928).

¹⁵⁸ Pougnet, J., *Compt. rend.*, **151**, 355, 566 (1910).

The photobromination of coumarin attains an equilibrium similar to that described by Berthoud and Nicolet for phenylcinnamionitrile. The rate of bromination is greater in carbon tetrachloride than in chloroform, but the reverse is true of the thermal reaction. Williams¹⁵⁹ finds that in ultraviolet light and with 60 molar concentrations of coumarin and bromine, an equilibrium results in 25 minutes in carbon tetrachloride at which time 85.6 per cent of the bromine had reacted. In chloroform, 65.8 per cent had reacted at equilibrium, reached in 45 minutes.

Considerable work has been done on the geometrical photoisomerizations of coumarin and its derivatives. Although Perkin had noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight, Stoermer¹⁶⁰ found the tendency the other way in the coumaric acid series, the stable form changing to the labile in ultraviolet rays. Coumaric acid yields 75 per cent of coumarin, and methylcoumaric acid yields 75 per cent of methylcoumarinic acid, while ethylcoumaric acid and acetylcoumaric acid are quantitatively changed to the corresponding coumarinic acids. Benzene or alcoholic solutions were used. Vaidya¹⁶¹ found the following quantum yields (3130 Å) for the transformation of coumaric acid: 0.005 molar, 0.031; 0.002 molar, 0.023.

Dey, Rao and Seshadri¹⁶² have pointed out that the esters undergo inversion more readily than the acids. The presence of a nitro-group in the benzene ring accelerates the transformation of both acids and esters but a methoxyl group has the opposite effect. An alcoholic solution of *o*-coumaric acid formed coumarin in 48-per cent yield after six hours of exposure to light and 65-per cent after 24 hours. The methyl and ethyl esters underwent 87- and 74 per cent conversion in 24 hours. Ordinary sunlight supplies the requisite energy for the transformation of the *trans* forms of the coumaric acids and their esters into the *cis* form with higher energy content.

OTHER AROMATIC COMPOUNDS WITH DOUBLE BONDS IN A SIDE CHAIN

Styrenes. Smakula¹⁶³ measured the absorption spectra of a number of polystyrenes of molecular weights 3,900 to 240,000. All showed an absorption band at 2600 Å, the intensity of which increased directly with the molecular weight. A comparison of their spectra with those of styrene and of ethylbenzene showed that the absorption bands belong to the phenyl radicals.

Obviously, stereoisomeric forms of styrene, phenylethylene, cannot exist because of the symmetry of the CH_2 . The possibility of photoreaction is therefore limited to polymerization. Stobbe¹⁶⁴ found that an equilibrium is set up between styrene and metastyrene. Styrene solution (5 per cent) showed the following changes in refractive index after 0, 20, 32, 95 and 230 hours of irradiation in Uviol tubes: 1.49883, 1.49911, 1.49939, 1.4994, 1.4994. Metastyrene showed the values: 1.50125, 1.50125, 1.50125, 1.50116, 1.50116. The irradiated solution of styrene gave a precipitate of metastyrene with alcohol; that of metastyrene decolorized permanganate, but the solutions kept in darkness did not.

Taylor and Vernon¹⁶⁵ found the photopolymerization could be accelerated by

¹⁵⁹ Williams, D. M., *J. Chem. Soc.*, 1383 (1929).

¹⁶⁰ Stoermer, R., *Ber.*, 42, 4865 (1909); 44, 637 (1911); *J. Chem. Soc.*, 98, II, 114 (1910).

¹⁶¹ Vaidya, B. M., *Proc. Roy. Soc.*, A129, 299 (1930).

¹⁶² Dey, B. B., Rao, R. H. R., and Seshadri, T. R., *J. Indian Chem. Soc.*, 11, 743 (1934); 12, 140 (1935); *Chem. Abs.*, 29, 4752 (1935).

¹⁶³ Smakula, A., *Angew. Chem.*, 47, 777 (1934).

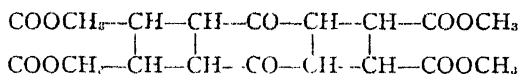
¹⁶⁴ Stobbe, H., *Ber.*, 47, 2701 (1914).

¹⁶⁵ Taylor, H. S., and Vernon, A. A., *J. Am. Chem. Soc.*, 53, 2527 (1931).

previous storage of the styrene in contact with oxygen. After 144 hours in contact with hydrogen, styrene polymerized when irradiated in Pyrex at a rate of 5.85 per cent per hour. When stored with oxygen, the rates were at the start, 6.39 per cent; 48 hours, 9.14 per cent; 96 hours, 9.15 per cent and 144 hours, 10.25 per cent per hour. Over oxygen, however, there is both oxidation as well as polymerization. To obtain the true rate of polymerization, hydrogen-distilled samples must be used. The temperature coefficient of polymerization is 1.33 per 10° between 30° and 70° and slightly less, 1.27, between 70° and 100°C. From viscosity measurements it seems that the aggregates formed at higher temperatures were of much larger size than those formed at low temperatures. Quantum yields of 4 at 3000 to 4000Å and 7.4 at 2536Å indicate a chain mechanism. Hydroquinone inhibits the change, partly by internal filtering and partly by deactivating collisions.

A low-boiling form of nitro- ω -bromostyrene, in which stereoisomerism is possible, is converted into a high boiling form by exposure to ultraviolet light.¹⁰⁶

bis-Distyrylketone is, according to Stobbe, Farber and Rau,¹⁰⁷ readily depolymerized to distyrylketone in the light of a mercury vapor lamp. Di-*p*-methoxystyrylketone is polymerized, but its addition compounds with uranyl chloride or stannic chloride do not appear to yield a dimer when exposed to light. Methyl- γ -ketopentadienedicarboxylate



is readily converted by light into a dimer not oxidized by permanganate and not capable of decolorizing bromine. Under analogous conditions, ethyl γ -ketopentadienedicarboxylate appears to suffer deep oxidative fission.

Exposure of an alcoholic solution of the yellow form of 2-hydroxystyrylmethyl ketone to rays of short wave-length from a quartz mercury vapor lamp for 24 hours produces a complete transformation to the colorless form.¹⁰⁸

Derivatives of benzoyl ethylene also exhibit geometrical isomerizations. *Trans*- α,β -*bis*-(2,4-dimethylbenzoyl)ethylene, on exposure to light, becomes coated with the *cis* isomer, which appears to revert slowly to the *trans* form on recrystallization.¹⁰⁹ α -Chlorodibenzoyl ethylene is transformed into the β -isomer by exposing a chloroform solution containing a trace of dibenzoyl- α,β -dichloroethane to strong sunlight for two hours. Dibenzoylbromoethylene is not, however, changed by sun light. Dibenzoyldichloroethylene exists in two forms: α , melting at 63-65°C. is more soluble in chloroform than the β -form, melting at 162°C. The former is transformed into the latter by strong sunlight. Similar transformation occurs also in the case of the dibromo-derivative.¹⁷⁰ Sunlight also isomerizes the yellow benzoyl ethylene phenyl sulfone, as well as β -bromo- β -benzoylvinyl phenyl sulfone, to colorless isomers with altered melting points.¹⁷¹

Von Halban and Geigel¹⁷² have shown that, in the case of tetrabenzoyl ethylene, an irreversible chemical change rapidly follows a primary phototropic process. Von Halban and Rast¹⁷³ state that when it is dissolved in acetic acid, concentrated sulfuric acid or sodium ethylate, a monohydrate can be crystallized out. On fur-

¹⁰⁶ Dann, A. T., Howard, A., and Davies, W., *J. Chem. Soc.*, 607 (1928).

¹⁰⁷ Stobbe, H., Farber, E., and Rau, F., *Ber.*, 58B, 1548 (1925).

¹⁰⁸ McGookin, A., and Heilbron, I. M., *J. Chem. Soc.*, 125, 2102 (1924).

¹⁰⁹ Coulson, E. A., *J. Chem. Soc.*, 1406 (1934).

¹⁷⁰ Conant, J. B., and Lutz, R. E., *J. Am. Chem. Soc.*, 47, 881 (1925).

¹⁷¹ Kohler, E. P., and Larsen, R. G., *J. Am. Chem. Soc.*, 57, 1448 (1935).

¹⁷² von Halban, H., and Geigel, H., *Z. physik. Chem.*, 96, 233 (1920).

¹⁷³ von Halban, H., and Rast, K., *Z. physik. Chem., Bodenstern-Festband*, 303 (1931).

ther illumination, a colorless powder, melting at 300°C., very slightly soluble and of unknown molecular weight is obtained, apparently as the result of an internal oxidation. The corresponding reduction product can not, however, be obtained. In indifferent solvents, a yellow substance is formed. The quantum yields for the conversion of *cis*- into *trans*-stilbene in hexane solutions by various mercury lines are, according to Smakula,¹⁷⁴ 3130A, 1.01; 3020A, 0.73; 2650A, 0.73; 2260A, 0.41; 1930A, 0.36.

Mercury arc irradiation of biphenylenethylene in ether completes its polymerization in two hours. The polymer when heated at 300-330° gives fluorene, methylfluorene, and a small quantity of a yellow hydrocarbon, C₂₇H₁₀, with blue fluorescence in benzene.¹⁷⁵

Chalcone. The condensation product of benzaldehyde and acetophenone, benzylideneacetophenone, is known as chalcone. On irradiation, it forms two dimers.¹⁷⁶ The dimer A, melting at 124°C. (truxinic ketone type) undergoes some decomposition (probably a depolymerization) with production of brown resins, when irradiated by sunlight or the mercury arc either as solid or in solution. The other dimer, B, (truxillic ketone type) is decomposed only to a slight extent by irradiation in the solid state or in chloroform solution.

Irradiation of chalcone in solution gives the dimer A only, the yields being about 30 to 35 per cent in the solvents acetic acid, chloroform, or ethanol. Less is formed in benzene solution. The yield is not affected by the presence or absence of oxygen, or hydrochloric acid or of erythrosine. In the presence of chlorophyll, however, the yield is cut to one-third its usual value and 1 to 1.5 per cent of dimer B is also formed.

Still a third dimer, C, was obtained to the extent of 7.5 per cent in one experiment in which a benzene solution was irradiated by a quartz mercury arc. Irradiation in the solid state or in suspension produces both the dimers A and B, the yield of the latter decreasing with the use of progressively shorter wave-lengths.

The results are to be compared with those of cinnamic acid and of the methyl esters of benzalpyruvic acid. With chalcone in solution, there is polymerization rather than isomerization, but the cinnamic acids in solution isomerize rather than polymerize. The production of the lower melting truxinic ketone type of dimer from chalcone in solution and of the higher melting truxillic ketone type in the solid state process agrees with the behavior of the benzalpyruvate esters.

The absorption spectra of chalcone, dihydrochalcone and the dimers conform to the general rule¹⁷⁷ that the curves of dimers lie between those of the monomer and of the saturated dihydro- compound. Stobbe and Bremer also reported data on various methyl and methoxy chalcones. In general, it was found that unsubstituted chalcone and all *p*- or *p'*-monosubstituted chalcones tended to polymerize in light. On the other hand, *pp'*-disubstituted ones resisted this process and in most instances exhibited a great tendency to resinification. Solid 3,4-methylenedioxychalcone was apparently unaffected.

No general relation between light-sensitivity and constitution could be found between the various chalcones and the corresponding cinnamic acids. Chalcones with an α -substituted ethylene, ArCH=CR-COAr, readily isomerize when R is a methyl or phenyl group, but not when it is an acetyl or COOC₂H₅. In neither case did polymerization occur. The only β -substituted chalcone examined (dypnone or β -methylchalcone) was unaffected by ultraviolet light when exposed alone or in solution. In the similarly constituted cinnamic acids, either α - or β -substitution generally hinders polymerization, although exceptions are known.

Exposure of the anti-oxime of chalcone to ultraviolet light produced a certain amount of discoloration but no polymerization. The α -semicarbazone, which melts at 168°C., yielded equal quantities of resin and unchanged product, but the form with melting point between 179° and 180°C. readily underwent a peculiar transformation to a yellow isomer.¹⁷⁸ It was shown later by Stobbe and Bremer¹⁷⁹ that both the α - and γ -chalcone

¹⁷⁴ Smakula, A., *Z. physik. Chem.* **25B**, 90 (1934).

¹⁷⁵ Wieland, H. and Probst, O., *Annalen*, **530**, 274 (1937).

¹⁷⁶ Stobbe, H., and Hensel, A., *Ber.*, **59**, 2254 (1926); Stobbe, H., and Bremer, K., *J. prakt. Chem.*, **123**, 1 (1929); *Chem. Abs.*, **24**, 92 (1930); *Brit. Chem. Abs.*, **1930A**, 1180.

¹⁷⁷ Stobbe, H., *Z. angew. Chem.*, **39**, 673 (1926). For studies on *o*-nitrochalcones, see Tănăsescu, I., and Baciuc, A., *Bull. soc. chim.*, **4**, 1742 (1937).

¹⁷⁸ See also Heilbron, I. M., and Wilson, F. J., *J. Chem. Soc.*, **101**, 1482 (1912).

¹⁷⁹ Stobbe, H., and Bremer, K., *J. prakt. Chem.*, **123**, 241 (1929).

semicarbazones, which are stable in darkness, become yellow when exposed to ultraviolet light, the change occurring readily in diffuse daylight in the case of the γ -compound. In alcohol or chloroform, both yellow forms give colorless solutions. These on concentration in darkness yield the colorless form, but in light the yellow form. The colorless forms give yellow solutions in alcoholic sodium alkoxide, sodium hydroxide or piperidine, acidification restoring the colorless form. They suggest that the yellow color in sodium alkoxide solution is not due to stereoisomerism as had been suggested by Heilbron and Wilson, but to salt formation within the urea portion of the molecule.

$R:N.NH.CO.NH_2 \longrightarrow R:NNH.C(OH):NH$ or $R:N.N:C(OH).NH_2$ in which R is $CHC_6H_5:CH.CC_6H_5:$. Similarly, the yellow forms obtained on exposure of the colorless semicarbazone are equilibrium mixtures of the keto-form with the *aci*-forms.

It was found that in general, the γ -forms of substituted chalcone semicarbazones are less light-stable than the α -forms and become colored in diffuse daylight. Both forms are colored by fifteen minutes of exposure to ultraviolet light. Comparison with the semicarbazone of 4'-methyl-dihydrochalcone and other saturated aromatic and aliphatic ketones and with various arylideneacetones showed that only the derivatives of unsaturated ketones become colored on exposure to ultraviolet light, or give colored solutions in sodium ethoxide, or enol tests with ferric chloride. The tautomeric change is therefore believed to be dependent upon the presence of conjugated double linkings.

Methyl benzalpyruvate, on exposure in dry form to sunlight, gives a small quantity of a polymeric ester, melting at $154^\circ C$. and an oil, which may be a mixture of isomers and decomposition products. In benzene solution there was also formed, as previously noted, a polymer melting at $117^\circ C$. The behavior of the higher-melting polymer led Reimer¹⁸⁰ to assign it a structure of the truxillic acid series, the lower-melting form being assigned to the truxinic acids. The formation of the latter was explained by assuming, as in the case of the cinnamic acids, that in solution isomerization first occurred, the product polymerizing. It was pointed out that it is unusual for polymerization of this type of substance to occur in solution, although a few cases had been described.¹⁸¹

It was found by Rice¹⁸² that the yellow methyl and ethyl esters of benzoylacrylic acids are transformed in sunlight into the corresponding colorless stereoisomeric esters. The reverse transformation takes place when solutions containing a trace of iodine or bromine are exposed to sunlight. The *p*-methoxybenzoyl (and ethoxy) acrylic esters behave similarly.

Bogert and Ritter¹⁸³ stated that β -benzoylacrylic acid is not isomerized by ultraviolet light, but Rice later states¹⁸⁴ that methyl *p*-phenoxybenzoylacrylate is changed in benzene solution by sunlight from the stable yellow form to the labile, colorless isomer. The reverse change is effected by the addition of a trace of iodine to the benzene solution. When the yellow modification is exposed as a thin layer of solid, it is rapidly converted to a colorless polymer, $C_{31}H_{28}O_4$. Rice, however, agrees that free *p*-phenoxybenzoylacrylic acid is not changed by sunlight in benzene solution. In cool weather, it is also unchanged when exposed as a solid, but in hot weather it becomes coated with a carrot-colored layer. She also shows that sunlight transforms the yellow form of methyl bromo-5-bromo-2,4-dimethoxybenzoylacrylate into the colorless form.¹⁸⁵ da Costa¹⁸⁶ obtained *cis*- α -methyl- β -anisylacrylic acid and *cis*- β -methyl- β -anisylacrylic acid by irradiation of aqueous solutions of the sodium salts of the corresponding *trans*-acids.

¹⁸⁰ Reimer, M., *J. Am. Chem. Soc.*, **46**, 783 (1924).

¹⁸¹ Ciamician, G., and Silber, P., *Ber.*, **42**, 1388 (1909); Stobbe, H., and Rücker, C., *Ber.*, **44**, 869 (1911); Reimer, M., and Keller, E., *Am. Chem. J.*, **50**, 157 (1913).

¹⁸² Rice, G. P., *J. Am. Chem. Soc.*, **45**, 222 (1923); **46**, 214, 2319 (1924).

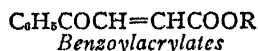
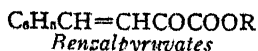
¹⁸³ Bogert, M. T., and Ritter, J. J., *J. Am. Chem. Soc.*, **47**, 526 (1925).

¹⁸⁴ Rice, G. P., *J. Am. Chem. Soc.*, **48**, 269 (1926).

¹⁸⁵ Rice, G. P., *J. Am. Chem. Soc.*, **50**, 1481 (1928).

¹⁸⁶ da Costa, R. M., *Compt. rend.*, **190**, 1996 (1934).

Reimer¹⁸⁷ discussed the difference in behavior of the benzalpyruvates and the benzoylacrylic acids just described.



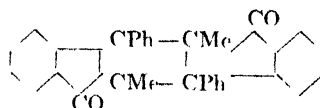
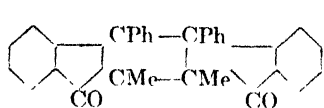
The system of conjugated double bonds is the same in each case, but its relation to the phenyl and carboxyl groups differs. The representatives of the first polymerize but those of the second isomerize instead. Miss Reimer later found¹⁸⁸ that benzalpyruvic acids in which methoxyl groups are substituted in the nucleus are less affected by sunlight. The most active substance is colorless β -bromo benzalpyruvic acid.¹⁸⁹ Its benzene solutions become lemon-yellow in two or three days in diffused light. Direct sunlight fades this to colorless, the color reappearing after removal from sunlight. The color change can be repeated many times and is remarkably sensitive to changes in intensity. From the decolorized solutions, a white crystalline dimer was isolated. It became brilliantly yellow overnight. The yellow form is regarded as a geometrical isomer of the original acid.

In stoppered tubes, there is also a photodecomposition of some of the compounds producing hydrogen bromide. The yellow form and the polymer are not obtained, but brown decomposition products result. Exposure of the original acid without a solvent yields slowly, without the formation of a colored intermediate, a crystalline dimer isomeric with that formed in benzene solution.

In the presence of oxygen, the benzene solution forms, in addition to the dimer a bromoacid, apparently by the addition of the elements of hypobromous acid to the original unsaturated acid. When the benzene contains moisture, colorless crystals of a saturated, bromine-free acid, $\text{C}_{10}\text{H}_{10}\text{O}_6$, are also formed by photochemical "hydroxylation" at the double bond.

The polymerization products are cyclobutane derivatives. Ellingboe and Fuson¹⁹⁰ found that ultraviolet light has little or no effect on *trans*-1,2-dibenzoylcyclobutane in benzene. According to Vorländer and Daehn¹⁹¹ 7-phenylheptatrienic acid and its sodium salt in aqueous suspension are strikingly stable, ultraviolet light decomposing only a small portion.

In benzene solution,¹⁹² 3-phenyl-2-methylindone gives rise to two diphenyldimethyltruxones, one being white and melting at 307-308°C. and the other pale canary-yellow, melting at 259-260°C.



These compounds react with concentrated sulfuric acid to form 3-phenyl-2-methylindone. When the latter is exposed in benzene solution to the action of ordinary

¹⁸⁷ Reimer, M., *J. Am. Chem. Soc.*, **46**, 783 (1924).

¹⁸⁸ Reimer, M., and Kamerling, H. H., *J. Am. Chem. Soc.*, **55**, 4643 (1933); Reimer, M., Tobin, E., and Schaffner, M., *Ibid.*, **57**, 211 (1935).

¹⁸⁹ Reimer, M., *J. Am. Chem. Soc.*, **58**, 1108 (1936).

¹⁹⁰ Ellingboe, E., and Fuson, R. C., *J. Am. Chem. Soc.*, **56**, 1774 (1934).

¹⁹¹ Vorländer, D., and Daehn, E., *Ber.*, **62B**, 545 (1929).

¹⁹² DeFazi, R., *Gazz. chim. ital.*, **54**, 85, 1000 (1924); **57**, 551 (1927).

sunlight, the truxone melting at 307-8°C. is formed, together with what appeared to be a third isomer, yellow crystals of melting point 174-176°C. A third diphenyl-truxone, $C_{30}H_{20}O_2$, yellow needles, m.p. 184-5°C., is obtained when the colorless isomers formed by treating ethyl β,β -diphenyl-lactate with concentrated sulfuric acid are exposed in benzene solution to ultraviolet rays. Ethylphenylindone does not give truxones when irradiated. Prolonged action of ultraviolet light on the 307-8°C. isomer of dimethyldiphenyltruxone in benzene converts it into methylphenylindone.

Bodforss¹⁹³ found that benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α -hydroxystyryl ketones with increasing readiness when their solutions in methyl alcohol are exposed to a mercury lamp. The yields of the isomers are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can be isolated.

Some of these transformations are phototropic, that is, the changes produced by light are reversed in darkness. This is notably the case with the fulgides studied particularly by Stobbe.¹⁹⁴ These are aryl derivatives of butadienedicarboxylic acid. Triphenylfulgide forms orange-red crystals which become dark brown in sunlight or in the rays of an arc lamp and which revert to their original color in darkness. The brown and orange forms seemed to be chemically identical. If the phototropic change is frequently repeated, the difference between the shades of the two forms becomes gradually less, a chemical change taking place which leads finally to the conversion of the fulgide into a new substance, the photoanhydride.

Phototropic change in these compounds was observed only in the case of the lemon-yellow to orange-red diaryl and the orange-red to dark red triarylfulgides; the colorless aliphyl, greenish-yellow to yellow monoaryl and red, purple-red or brown or tetraarylfulgides are not phototropic. The modifications of a phototropic substance can exist in the pure state only during exposure to the wave-length of light which forms them since they revert in darkness to a mixture or solid solution of more than one form. The equilibrium between the two modifications in a mixture depends on the wave-lengths of light (and their relative intensities) to which it is exposed.

The phototropy of other substances than the fulgides has also been studied by Stobbe.¹⁹⁵ Red and blue rays have no action in reversing the color change produced by ultraviolet light on colorless β -tetrachloro- α -ketonaphthalene, only yellowish-green and yellowish rays being effective. A complete discussion of the many instances of phototropy would consume much space.¹⁹⁶

STEREISOMERISM OF OXIMES

Stereoisomeric changes about the carbon-nitrogen double bond in the benzald-oximes also occur. Ciamician and Silber¹⁹⁷ showed the nitrobenz-*syn*-aldoximes to be changed to the *anti* form when their benzene solutions were exposed in glass tubes to sunlight. (It must be noted that these and other workers used the configurations in the sense opposite to that at present accepted. Thus, they stated

¹⁹³ Bodforss, S., *Ber.*, **51**, 214 (1918); (*Chem Abs.*, **12**, 2554 (1918); *J. Chem. Soc.*, **114**, 1, 232.

¹⁹⁴ Stobbe, H., *Annalen*, **359**, 1 (1908); *J. Chem. Soc.*, **94**, 11, 339 (1908).

¹⁹⁵ Stobbe, H., *Ber. Verhandl. Sachs. Akad. Wiss. Leipzig*, **74**, 161 (1922); (*Chem Abs.*, **17**, 3020 (1923)).

¹⁹⁶ For details, consult the review articles cited in Chapter 16. For benzylidene-, anisylidene- and cumylylidenehydrazones, see Biltz, H., and Wienands, A., *Annalen*, **308**, 1 (1899); *J. Chem. Soc.*, **76**, 910 (1899); tetraphenyldihydrotriazine, v. Walther, R., *J. Chem. Soc.*, **84**, 1, 582 (1903); ethyl oxaliso-butyrate, Wislicenus, W., and Kiesewetter, M., *J. Chem. Soc.*, **74**, 1, 240 (1898); α -azoxynaphthalene, Cumming, W. M., and Steel, J. K., *J. Chem. Soc.*, **123**, 2464 (1923); tetrahydrozolethylene, von Halban, H., and Geigel, H., *Z. physik. Chem.*, **96**, 233 (1920); aminoaryldisulfioxides, (Child, R., and Smiles, S., *J. Chem. Soc.*, 2696 (1926); diphenylacyldiphenylmethane, de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935). For further data on the fulgides, see Dietzel, R., and Naton, J., *Ber.*, **58B**, 1314 (1925); Stobbe, H., Ljungren, G., and Freyberg, J., *Ber.*, **59B**, 265 (1926); α - γ -diphenylallyl ether, Shoppee, C. W., *J. Chem. Soc.*, 2567 (1928). For "reversed phototropy," see Heilbron, I. M., and Wilson F. J., *J. Chem. Soc.*, **105**, 2892 (1914) and Heilbron, I. M., Hudson, H. E., and Huish, D. M., *ibid.*, **123**, 2273 (1923).

¹⁹⁷ Ciamician, G., and Silber, P., *Ber.*, **36**, 4268 (1903).

that the *anti* forms were converted to the *syn* forms.) Ciusa¹⁹⁸ reported similar changes in the case of *p*-chloro- and 3-nitro-*o*-methoxybenz-*syn*-aldoximes. He was unable to observe the conversion in the case of unsubstituted benz-*syn*-aldoxime or of 3,4-methylenedioxy-*syn*-aldoxime, and inferred that the presence of a negative substituent is necessary for the change to occur. By the use of a quartz mercury arc, however, Brady and McHugh¹⁹⁹ showed that this is not the case and that the conversions can be effected. The change occurred in all but two of a series of 24 aldoximes and their derivatives. 3,4-Dimethoxybenz-*syn*-aldoxime underwent no change²⁰⁰ and 5-bromo-3,4-dimethoxybenz-*syn*-aldoxime suffered demethylation to 5-bromo-3-methoxy-4-hydroxybenz-*syn*-aldoxime. The methyl ether of benzaldoxime is decomposed by ultraviolet with the formation of benzonitrile, but the methyl ether of *m*-nitrobenzaldoxime undergoes no change. The methyl ethers of *m*- and *p*-nitrobenz-*syn*-aldoximes are partially isomerized, confirming earlier results obtained with sunlight,²⁰¹ but not so rapidly or completely as in the case of the oximes themselves. In subsequent work, Brady and Klein²⁰² succeeded in effecting the conversion in the α -*O*-*p*-nitrobenzyl ethers of *o*-, *m*- and *p*-aldoximes, of 3,4-methylenedioxybenzaldoxime, of *o*- and *p*-methoxybenzaldoxime of 3-nitro-4-methoxybenzaldoxime, and of 5-nitro-2-methoxybenzaldoxime, as well as in α -*O*-methyl-6-nitro-3,4-methylenedioxybenzaldoxime. Although similar treatment of the α -*O*-methyl-3-nitro-4-methoxybenzaldoxime resulted in partial inversion, the product could not be separated into its components. Brady and Peakin²⁰³ found that, apart from slight but profound decomposition, *m*-nitrobenzodimethyl amidoxime is unchanged by exposure, in benzene solution in a silica vessel for 48 hours to the light of a quartz mercury lamp.²⁰⁴

The isomeric changes of the semicarbazones, particularly of cinnamaldehyde have been discussed in previous paragraphs and it has been pointed out that some workers believe the changes can be attributed to tautomerism within the urea portion of the molecule without the necessity of considering stereoisomerism about the double bonds in other portions of the molecule. On exposing solutions of the semicarbazones of dypnone and phenyl- β -phenylstyryl ketone, and the mesityl oxide- δ -phenylsemicarbazones to a quartz mercury lamp, Wilson and Macaulay²⁰⁵ observed that stereoisomers are formed. Attempts to prepare stereoisomers of the semicarbazones of benzylacetone, benzylacetophenone, methyl styryl ketone and styrylisobutenyl ketone gave negative results.

Phototropy is observed in many semicarbazones. Gheorghiu and Arwentiew²⁰⁶ find the semicarbazone resulting from the condensation of methyl isobutyl ketone with anisaldehyde to become colored in diffused light, a general property of the semicarbazones of the aldehyde condensation products with ketones in the α - but not in the γ -position. Although the semicarbazones of ethylenic ketones of the type $\text{ArCH}=\text{CHCOR}$, in which Ar is aryl and R either alkyl or aryl, resulting from the alkaline condensation of methyl ketones with aromatic aldehydes are phototropic, those of the ketones $\text{ArCH}=\text{CRCOCH}_3$

¹⁹⁸ Ciusa, R., *Atti R. Accad. Lincei*, **15**, ii, 721 (1906).

¹⁹⁹ Brady, O. L., and McHugh, G. P., *J. Chem. Soc.*, **125**, 547 (1924).

²⁰⁰ See Brady, O. L., and Dunn, F. P., *J. Chem. Soc.*, **123**, 1790 (1923).

²⁰¹ Brady, O. L., and Dunn, F. P., *J. Chem. Soc.*, **103**, 1624 (1913).

²⁰² Brady, O. L., and Klein, L., *J. Chem. Soc.*, **874** (1927).

²⁰³ Brady, O. L., and Peakin, F. H., *J. Chem. Soc.*, **2269** (1929).

²⁰⁴ For absorption data on various oximes and semicarbazones, see Ramart-Lucas, Mme., and Grumez M., *Bull. soc. chim.*, **53**, 753 (1933); Ramart-Lucas, Mme., and Bruzau, Mme., *Bull. soc. chim.*, **11**, 119 (1934). For thiocyanacetoneoxime, Ponomarev, F. G., Alpatov, D. M., and Strepetov, N. P. *Acta Univ. Voynegiensis*, **9**, No. 3, 132 (1937); *Chem. Abs.*, **32**, 7021 (1938).

²⁰⁵ Wilson, F. J., and Macaulay, R. M., *J. Chem. Soc.*, **125**, 841 (1924).

²⁰⁶ Gheorghiu, C. V., and Arwentiew, B., *Ann. sci. Univ. Jassy*, **16**, 536 (1931); *Chem. Abs.*, **26**, 4804 (1932); see also Dickinson, R., Heilbron, I. M., and Irving, F., *J. Chem. Soc.*, **1888** (1927).

obtained by acid condensation are stable to light.²⁰⁷ Since the phototropy is connected with the presence of double bonds conjugated with the benzene nucleus, all changes disturbing the conjugation tend to diminish or eliminate the phenomenon. It is probable that the phototropic change consists in a shift of the valence electrons brought about by the action of light.

The thiosemicarbazones and δ -phenylsemicarbazones of the ethylenic ketones of the type $\text{ArCH}=\text{CHCOR}$ are always phototropic.²⁰⁸

AROMATIC AMINES

The spectrum of aniline vapor includes 185 lines and bands between 1980 and 2632 Å and a continuous zone from 2632 Å.²⁰⁹ Savard found for the excitation energies of three electronic states 97.9, 99.2 and 102 kcal. The energy of dissociation into $\text{C}_6\text{H}_5\text{NH}$ and a hydrogen atom is 108 kcal.²¹⁰

By studying the change in the ultraviolet absorption of solutions with change in pH, Hammett, Dingwall and Flexser²¹¹ determined its dissociation constant. The well-known photochemical discoloration of aniline²¹² is believed to be an oxidation. It is furthered by the presence of *o*- and *p*-phenylenediamine as impurities, but is retarded by the *m*-isomer and is almost completely inhibited in the absence of oxygen. It is also retarded by minute amounts of sodium sulfide or oxalic acid, or by contact with emery-surfaced zinc or iron plates, either untreated or previously boiled with 20-per cent sodium sulfide. On the other hand, if iron plates are cleaned by heating with dilute sulfuric acid, they accelerate the reaction even though they have been treated with sodium sulfide. Mild heating over a gas flame somewhat restores the preserving action. Partially rusted iron plates after boiling with 20-per cent sodium sulfide also retard the oxidation. These experiments were conducted to develop methods for the storage and transportation of aniline in iron drums. In the method recommended, the drums were flushed with hot water, and without further cleaning were boiled with 5- to 20-per cent sodium sulfide, sealed, allowed to cool, emptied, flushed with water and then twice with aniline and filled as soon as possible to avoid oxidation of the iron sulfide film. Yamanaka²¹³ believes light of the range 5100 to 3000 Å, and especially 4957 to 4300 Å to be most effective in producing the color. On the other hand, Freytag,²¹⁴ by exposing strips of hardened filter paper impregnated with aqueous or alcoholic solutions of 18 primary amines behind a quartz spectrograph, found the majority of them to be sensitive only to ultraviolet light of wave-lengths less than 3130 Å. The intensity of the color developed varied greatly with the wave-length employed. He finds²¹⁵ ultraviolet to markedly accelerate aniline black dyeing. Photographic negatives may be printed on cotton fabric impregnated with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous potassium chlorate solution per 30 cc.,

²⁰⁷ Gheorghiu, C. V., *Bull. soc. chim.*, **53**, 1441 (1933).

²⁰⁸ Gheorghiu, C. V., *Bull. soc. chim.*, **1**, 97 (1934).

²⁰⁹ Savard, J., *Compt. rend.*, **190**, 678 (1930); *Bull. soc. chim.*, **53**, 1404 (1933).

²¹⁰ See also, Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, Suppl. 284 (1934). For a comparison of the spectra of aniline and acetanilide, see Klingstedt, F. W., *Z. physik. Chem.*, **1B**, 74 (1928). Benzylamine, Ley, H., and Volbert, F., *Ber.*, **59B**, 2119 (1926). Nitrosodimethylaniline, Custers, J. F. H., and Dippel, C. J., *Z. Physik*, **86**, 516 (1933). Nitroanilines, Glotz, G., *Bull. soc. chim.*, **1**, 1148 (1934). Toluidines, Morton, R. A., and McGookin, A., *J. Chem. Soc.*, 901 (1934). Arylamines, Ramart-Lucas, Mme., and Wohl, Mlle., *Compt. rend.*, **196**, 1804 (1933). For fluorescence studies on amines, see Lumière, A., Lumière, L., and Seyewetz, A., *Bull. soc. chim.*, **37**, 700 (1925).

²¹¹ Hammett, L. P., Dingwall, A., and Flexser, L., *J. Am. Chem. Soc.*, **56**, 2010 (1934).

²¹² Bulich, P. K., *Anilinokrasochynaya Prom.*, **3**, 405 (1933); *Chem. Abs.*, **28**, 1335 (1934).

²¹³ Yamanaka, T., *Bull. Inst. Phys.-Chem. Research (Tokyo)*, **14**, 396 (1935); *Chem. Abs.*, **30**, 1754 (1936).

²¹⁴ Freytag, H., *Z. wiss. Phot.*, **33**, 33 (1934); *Brit. Chem. Abs.*, **1934A**, 740.

²¹⁵ Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

exposing for fifteen minutes to ultraviolet light and washing away the unchanged aniline with water.

The reactions between aniline and nitrobenzene which occur during a five months' exposure to summer sunlight in sealed tubes have been studied by Vecchiotti and Piccinini.²¹⁶ The liquid became red-brown but was neutral in reaction and evolved no gas. Among the compounds identified were, besides unchanged nitrobenzene and resin, *o*-hydroxyazobenzene, azoxybenzene and a small quantity of *p*-aminophenol. The results are explained by regarding the initial reaction as a simultaneous oxidation and reduction of nitrobenzene forming nitrosobenzene and phenylhydroxylamine. The nitrosobenzene reacts with the phenylhydroxylamine to yield water and azoxybenzene, the latter then transforming into *o*-hydroxyazobenzene. The great tendency of phenylhydroxylamine to change to *p*-aminophenol accounts for the presence of this material. Decomposition products of nitrosobenzene probably enter into other secondary reactions.

In the reaction between toluene and nitrobenzene there were obtained,²¹⁷ in addition to benzoic acid and *p*-aminophenol, aniline and azoxybenzene. The benzoic acid is formed by oxidation of toluene by nitrobenzene which is reduced to nitrosobenzene. A molecule of unaltered nitrobenzene reacts with three of benzaldehyde, an intermediate oxidation product, to produce two of benzoic acid and one of benzoylaniline. The latter is then hydrolyzed to aniline and benzoic acid. Benzoylaniline also may be formed along with benzoic acid by the interaction of nitrosobenzene with two molecules of benzaldehyde.²¹⁸ Azoxybenzene may be formed either by the interaction of nitrosobenzene and benzaldehyde or, by analogy with the reaction of nitrosobenzene and phenylhydroxylamine, by the interaction of nitrosobenzene and benzoylphenylhydroxylamine. It might also be produced by a reaction between nitrosobenzene and *p*-OHC₆H₄NHCOC₆H₅. The compounds required for the last two processes were not isolated although their formation is conceivable. According to Knipscheer,²¹⁹ *o*-hydroxyazobenzene is formed by the action of light on azoxybenzene, but it was not identified by the Italian observers. The aniline is partly oxidized to phenylhydroxylamine, which under the influence of light, forms *p*-aminophenol.

The action of sunlight for six months on a mixture of *o*-nitrotoluene and aniline gave a product containing *p*-aminophenol, 2'-methylazoxybenzene, and an isomer of the latter, probably a benzeneazocresol.²²⁰

Plisov²²¹ made some preliminary experiments on the photochemical formation of salts of aromatic amines with alkyl halides in an attempt to determine whether the activation of the amine or of the halide is the determining factor in the reaction. Photochemical action is more evident in the combination of aniline with benzyl chloride than in the case of *o*-toluidine and benzyl chloride. In the former case, the yield in three hours increased from 15 per cent in darkness to 82 per cent under irradiation in a quartz vessel by an arc.

Migrations in N-Substituted Amines. Blanksma²²² has noted that acetylchloroaminobenzene is altered by light, following the general rule that the radicals

²¹⁶ Vecchiotti, L., and Piccinini, C., *Gazz. chim. ital.*, **61**, 626 (1931).

²¹⁷ Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **61**, 798 (1931).

²¹⁸ Bamberger, E., *Ber.*, **35**, 1606 (1902); Ciamician, G., and Silber, P., *Atti accad. Lincei*, **14**, 265 (1905).

²¹⁹ Knipscheer, H. M., *Rec. trav. chim.*, **22**, 1 (1903).

²²⁰ Vecchiotti, L., and Piccinini, C., *Gazz. chim. ital.*, **63**, 112, 319 (1933); *Brit. Chem. Abs.*, **A**, 602 (1934).

²²¹ Plisov, A. K., *Gazz. chim. ital.*, **59**, 200 (1929); *Chem. Abs.*, **23**, 4198 (1929).

²²² Blanksma, J. J., *Proc. K. Akad. Wetensch. Amsterdam*, **5**, 178 (1902); *J. Chem. Soc.*, **82**, II, 646 (1902).

Br, Cl, NO₂, NO and O, attached to nitrogen, change places, under the influence of sunlight, with a hydrogen atom in the nucleus. Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight,²²³ and had previously studied the thermal reaction for which Armstrong²²⁴ found a trace of hydrogen chloride essential. Mathews and Williamson²²⁵ have studied the reaction in solutions in benzene, alcohol and acetic acid, using a quartz mercury lamp. The solvent exerts a marked effect, but hydrochloric acid is not required for the photoreaction. The addition of water to an alcoholic or glacial acetic acid solution greatly diminishes the velocity of the photo-decomposition. In the absence of water, the reaction in these solvents proceeds without the action of radiation, after having been started in this manner. In the presence of water, this effect is lacking and the reaction is truly photochemical.

Porter and Wilbur,²²⁶ who presented data on the absorption of ultraviolet by acetylchloroaninobenzene and its rearrangement product, found the transformation to occur in the solid phase as well as in solution. Hodges²²⁷ found the rate of the change under the influence of the 3569Å line in eight solvents very slow in the complete absence of water. It is a chain reaction, the quantum yields being 5.6 in carbon tetrachloride, 15-18 in bromobenzene, 17 in chloroform, 22 in chlorobenzene, 29-33 in benzene, 108-116 in toluene, 156-163 in cyclohexane, and 188 in decalin. In closely related solvents, the reaction velocity diminished with increasing dielectric constant, surface tension and density.

Condensation Reactions of Amines. The condensation of *p*-phenetidine hydrochloride with epichlorohydrin to N,N-bis(γ -chloro- β -hydroxypropyl)-*p*-phenetidine is accelerated by sunlight.²²⁸

Qualitative observations on the nature of the products formed by the prolonged exposure to tropical sunlight of a number of organic compounds in 2 per cent solutions in water, dilute acid or alkali or alcohol have been recently reported by Malaviya and Dutt.²²⁹ Aniline in hydrochloric acid precipitated phenazine in 135 days, *o*-toluidine gave 1,5-dimethylphenazine, *m*-toluidine, 2,6-dimethylphenazine and *p*-toluidine probably gave 3,7-dimethylphenazine. Dimethylaniline did not change in 141 days and 1,3,4-xylylidine gave only a trace of precipitate in 121 days.

α -Naphthylamine probably gave α,β -dinaphthazine and β -naphthylamine probably β,β -dinaphthazine. *o*-Nitraniline was unaffected *p*-Nitrosodimethylaniline in aqueous solution was oxidized to *p*-nitrodimehtylaniline, but in dilute acid, it gave an unidentified precipitate and benzidine gave an unidentified phenazine. In dilute acid, *o*-phenylenediamine gave 2,3-diaminophenazine hydrochloride, the *m*-compound 2,6-diaminophenazine and the *p*-compound probably 3,6-diaminophenazine. *p*-Aminodimethylaniline gave an intensely violet solution of an unidentified azine dye. Aqueous *p*-amino-acetanilide gave diacetyl-*p,p'*-diaminodiphenylamine. 1,8-Diaminonaphthalene gave a brown precipitate, probably *peri*-dinaphthalene azotide. *o*-Aminophenol formed a red compound, C₂₄H₁₈N₃O₂, the *m*-compound an unidentified brown precipitate, and the *p*-compound a violet precipitate, probably *p,p'*-dihydroxydianilinoindophenol. *m*- and *p*-Hydroxydimethylanilines were unaffected. 1,5-Dimethoxyphenazine was formed from *o*-methoxyaniline,

²²³ Chattaway, F. D., and Orton, K. J. P., *Proc. Chem. Soc.*, **81**, 200 (1902).

²²⁴ Armstrong, H. E., *J. Chem. Soc.*, **77**, 1047 (1900).

²²⁵ Mathews, J. H., and Williamson, R., *J. Am. Chem. Soc.*, **45**, 2574 (1923).

²²⁶ Porter, C. W., and Wilbur, P., *J. Am. Chem. Soc.*, **49**, 2145 (1927).

²²⁷ Hodges, F. W., *J. Chem. Soc.*, 240 (1933).

²²⁸ Strukov, I. T., *Khim. Farm. Prom.*, No. 2, 11 (1934); *Chem. Abs.*, **28**, 5421 (1934).

²²⁹ Malaviya, B. K., and Dutt, S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 319 (1935); *Chem. Abs.*, **30**, 1056 (1936).

the 3,7-compound from the *p*-derivative and corresponding diethoxyphenazines were produced from the ethoxy-compounds. 2,4-Hydroxyphenylenediamine gave an unidentified phenazine. Aminobenzoic acid gave phenazine-1,5-dicarboxylic acid, the *m*-compound did not alter, but the *p*-acid in alkaline solution gave the sodium salt of *p,p'*-azobenzenedicarboxylic acid.

Vanillin, 2,4-dihydroxybenzaldehyde and *p*-dimethylaminobenzaldehyde were unchanged. Aqueous *p*-aminobenzaldehyde hydrochloride gave *p,p'*-dialdehyde-azobenzene.

Aqueous 1-per cent eosin was decolorized in 75 days, giving hydrogen bromide and a precipitate of 2,4-dibromobenzoylbenzoic acid. Similarly erythrosine gave hydrogen iodide and probably 2,4-diiodobenzoylbenzoic acid. *p*-Aminoacetophenone gave an unidentified precipitate, capable of reducing ammoniacal silver nitrate, but gallacetophenone was unaffected. Phenylhydrazine evolved nitrogen and formed an unidentified, apparently heterocyclic nitrogen compound. 2-Aminothiazole gave a trace of a phenazine derivative. Aqueous thiocarbamide gave sulfur and carbamide in 46 days. α -Benzildioxime in dilute alkali gave 3,4-diphenylfurazan in 35 days.

Color Reactions of Amines. Schall²³⁰ proposed to test for ultraviolet rays by their ability to form a blue coloration on filter paper impregnated with *p*-phenylenediamine nitrate (2/3*N*) and dried. Such paper is sensitive only to wave-lengths shorter than 3130Å. Diffused daylight produces only a pale gray tint but a quartz mercury lamp produces a blue color in an instant. Mott and Bedford²³¹ made the paper by impregnating white blotting paper in a solution of 1 g. *p*-phenylenediamine, 3 cc. of water and 2 cc. of nitric acid, s.g. 1.21, and drying one-half hour in a steam oven.

Freytag²³² states also that irradiation of moist filter paper or cotton fabric impregnated with solution containing about 0.1 per cent of either phenylenediamine, or their mixtures, resulted in yellow to brown color formation due to oxidation of the base. This was assisted by the presence of 0.1 per cent sodium nitrate and potassium nitrate. The resulting colors were faster to washing when aniline was also present. The process could be adapted to the production of photographic prints on fabric.

Nile-blue, brilliant green, Capri-blue, phenosofranine, fuchsin and pinakryptol-green are negative catalysts toward the photochemical decomposition of "Aktivin," sodium *p*-toluenesulfonchloroamide, in methanol solution.²³³ Malachite-green had no effect, and pinakryptol-yellow and methylene-blue were positive catalysts, even in darkness.

The photochemical oxidation of aqueous solutions of benzidine in the presence of eosin is accelerated by manganese salts and by iron and copper salts in decreasing quantities.²³⁴ Eosin, chlorophyll and the fluorescent derivatives of the latter bring about the oxidation of benzidine in methanol. Green leaves in water solutions of benzidine also bring about its oxidation when illuminated.

Picric acid, in solutions at pH 13.0, is decomposed in ultraviolet light to give picramic and isopurpuric acids, nitrous acid, ammonia and hydrogen cyanide. The

²³⁰ Schall, C., *Photograph. Wochenblatt*, 33, 321 (1907); *Chem. Ztg.*, 34, 267; *Z. physik. Chem. Unterr.*, 21, 389 (1908).

²³¹ Mott, W. R., and Bedford, C. W., *J. Ind. Eng. Chem.*, 8, 1029 (1916).

²³² Freytag, H., *Melliand. Textilber.*, 13, 322 (1932); *Chem. Abs.*, 27, 1834 (1933).

²³³ Milbauer, J., *Phot. Korr.*, 71, 94 (1935); *Brit. Chem. Abs.*, A, 1468 (1935); *Chem. Listy*, 29, 267 (1935); *Chem. Abs.*, 30, 1661 (1930).

²³⁴ Noack, K., *Phot. Korr.*, 62, 73 (1926); *Chem. Abs.*, 21, 1409 (1927).

usual yellow form present at lesser pH values is unaffected.²³⁵ An analogous reaction occurs with 2,5-dinitrophenol. *o*- and *p*-Nitrophenols, 2,4- and 2,6-dinitrophenols and 2,4-dinitro-*o*-cresols decompose at reactions at which the red forms exist, the rate increasing with the pH. These darken with the formation of an amino- group.

Textiles of animal or vegetable fibers impregnated with nitrophenols, nitroamines, or even colorless nitro- compounds, turn brown when exposed to daylight or ultraviolet rays.²³⁶ Reduction apparently takes place, as reducing agents hasten, and oxidizing agents retard, the effect. The brown substance thus formed from picric acid on calico was isolated, by extraction with alkali and precipitation with acid, and found to contain nitro- or nitroso- groups, but no amino- group. This substance may be an azo- compound derived from an azoxy-reduction product of picric acid.

Azo, Diazo and Related Compounds. Knipscheer²³⁷ has shown that azoxybenzene is converted by light into *o*-hydroxyazobenzene. He obtained the latter in poor yield (10.3 per cent) and with much loss of material by volatilization (39.7 per cent) by exposing sheets of filter paper impregnated with azoxybenzene to sunlight for five weeks. Cumming and Ferrier,²³⁸ who believed the loss by volatilization could be obviated by making the exposures in solution, employed a mercury vapor lamp as source. The best results (28.0 per cent) were obtained by 50 hours' exposure in absolute ethanol and the smallest (7.7 per cent) with benzene as solvent. Increase of temperature improved the yield only slightly, but materially increased the loss of azoxybenzene by volatilization. The transformation also takes place in sunlight, but cannot be effected by an ordinary electric light.

The action of light on the α -isomer of benzeneazoxy-*p*-toluene, $\text{NC}_6\text{H}_4\text{O}=\text{N}.\text{C}_6\text{H}_4\text{CH}_3$ yields a red substance, probably an *o*-hydroxy- compound.²³⁹ The β -isomer, $\text{NC}_6\text{H}_4=\text{NO}.\text{C}_6\text{H}_4\text{CH}_3$, very slowly turns yellow.

Cumming and Ferrier also obtained hydroxyazo- compounds from 2,2'- and 3,3'- and 4,4'-azoxytoluenes, 4,4'-dichloroazoxybenzene and 2,2'-diamino-4,4'-azoxytoluene. 4,4'-Azoxyanisole, 4,4'-azoxyphenetole, and 4,4'-dinitroazoxybenzene reacted slightly or not at all. In the case of 2,2'-azoxytoluene, products of widely different melting points were obtained in alcohol and in benzene as solvents. The hydroxyazo- compounds were obtained as red needles of varying solubility in sodium hydroxide solution. In cases in which the orientation could be determined, the hydroxyl group appeared to enter the benzene nucleus in the ortho position with respect to the azo-group.²⁴⁰

The decomposition of a 0.4 per cent solution of diazosulfanilic acid in ultraviolet light is proportional to the time of irradiation until 90 per cent has been decomposed; the remainder condenses with the phenol produced.²⁴¹ At pH values less than 7, the diazo- solution is very sensitive to light, but relatively stable to heat, while in alkaline solutions, the reverse is true. Similar results are obtained at 35°, 56°, 80° and 100°C., but when the temperature approaches that at which thermal decomposition of the diazo- compound occurs, this action predominates. Substitution of negative

²³⁵ Molnar, J., *Compt. rend.*, **201**, 1482 (1935).

²³⁶ Seyewetz, A., and Mounier, D., *Compt. rend.*, **185**, 1279 (1927).

²³⁷ Knipscheer, H. M., *Rec. trav. chim.*, **22**, 1 (1903).

²³⁸ Cumming, W. M., and Ferrier, G. S., *J. Chem. Soc.*, **127**, 2374 (1925).

²³⁹ Bigiavi, D., and Sabatelli, V., *Gazz. chim. ital.*, **57**, 557 (1927); *Chem. Abs.*, **22**, 395 (1928).

²⁴⁰ See also Ramsperger, H. C. for some determination of reaction rates for the thermal and photochemical decomposition of azo- compounds, *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

²⁴¹ Seyewetz, A., and Mounier, D., *Compt. rend.*, **186**, 953 (1928); *Bull. soc. chim.*, **43**, 827 (1928); *Brit. Chem. Abs.*, **1928A**, 493.

radicals in the benzene nucleus, which increases the stability of the diazo- compound to heat, decreases its stability to light, the order of increasing stability being p -OH (anhydride) < p -SO₃H (anhydride) < p -COOH (anhydride) < p -Cl (chloride) < p -NO₂ (chloride) < benzenediazonium chloride. Decomposition is complete only in the first two cases. The effect of the nitro- group is the same in the ortho, meta and para positions. Decomposition by light of the diazo- compounds derived from sulfanilic acid, p -aminophenol, and aniline yields the corresponding phenol as in thermal decomposition; the derivative of p -aminobenzoic acid yields p -hydroxy- and p -chlorobenzoic acids, while from the brown precipitate obtained by decomposition of nitrobenzenediazonium chlorides is isolated a substance which is probably dinitrodiphenyl ether.

By comparing the absorption spectra before and after photolysis, Fukushima and Horio²⁴² concluded that the photodecomposition of diazobenzene sulfonic acid differs from the thermal reaction. It is effected by radiations of wave-length shorter than 3800Å. The reaction is of zero order. An inner filter, such as quinine sulfate, retards the photolysis. The effects of temperature are complex.

Azo compounds may be photosensitized by zinc oxide, according to Fukushima, Horio and Omori.²⁴³ In dilute alcoholic solution and an oxygen-free atmosphere in the presence of zinc oxide, azobenzene was reduced almost quantitatively to hydrazobenzene, but with pure oxygen there was no reduction in six months.²⁴⁴

Lyashenko and Kirzner²⁴⁵ carried out the photolysis of phenyldiazonium chloride and its o -, m -, and p -substituted derivatives under exactly similar conditions by exposing the diazo- solutions for three hours to the action of daylight and the light of a mercury vapor lamp. The nitrogen eliminated was measured. They found that substitution in the meta position either increases the stability of aniline to light or has no influence. Substitution in the ortho and para positions decreases it. The ethoxy- group in the para position has no effect.

Other Compounds. The condensation products of aromatic thiohydrazide with aldehydes, ketones, and sugars on irradiation with the lines 6250, 5950 and 5430Å exhibit a rapid drop of the rotatory power from a high value in one direction through zero to a maximum in the opposite direction.²⁴⁶ Continued exposure causes the rotation again to reach zero and then to attain a maximum in the initial direction, after which it slowly drops off to zero. This is explained as a combination of partial racemization, *cis-trans* isomerization and a change in structure, all of which are affected by light.

2,2'-dinitro-5,5'-dimethoxydiphenyl disulfide rapidly turns yellow in sunlight.²⁴⁷

²⁴² Fukushima, I., and Horio, M., *J. Soc. Chem. Ind. Japan*, **34**, Suppl. binding, 367, 372, 374 (1931), *Chem. Abs.*, **26**, 2377 (1932).

²⁴³ Fukushima, I., Horio, M., and Omori, M., *J. Soc. Chem. Ind. Japan*, **35**, Suppl. binding, 398 (1932); *Chem. Abs.*, **26**, 5848 (1932).

²⁴⁴ The formation of equilibrium between *cis* and *trans* forms of azobenzene can be activated by light Hartley, G. S., *Nature*, **140**, 281 (1937); von Auwers, K., *Ber.*, **71B**, 611 (1938); Cook, A. H., *J. Chem. Soc.*, 876 (1938).

²⁴⁵ Lyashenko, V. D., and Kirzner, N. A., *Anilinokrasochnaya Prom.*, **4**, 272 (1934); *Chem. Abs.*, **28**, 7164 (1934).

²⁴⁶ Lifschitz, I., and Froentjes, W., *Rec trav chim*, **55**, 753 (1936)

²⁴⁷ Hodgson, H. H., and Handley, F. W., *J. Chem. Soc.*, 542 (1926).

Chapter 26

Compounds with Condensed Ring Systems

NAPHTHALENE DERIVATIVES

There appear to be no descriptions of photochemical reactions of naphthalene. However, its absorption spectrum and also spectra of many of its alpha- and beta-derivatives have been investigated by de Laszlo.¹ Its vapor exhibits about 400 sharp narrow bands with fine structure between 3200 and 2820A and a group of broad continuous bands without fine structure between 2820 and 2500A.

Although naphthalene vapors are stable to the light of the quartz mercury arc, 1,2- and 1,4-dihydronaphthalenes quickly decompose to naphthalene. Tetralin decomposes more slowly, forming unidentified polymerization products.²

A number of nitro- derivatives of naphthalene are light-sensitive, producing brown colors which result from the reduction of nitro- groups. Much work has been devoted to the study of the mutual effects of nitro- and sulfonic acid groups in various positions upon the light sensitivity. One of the earliest instances observed was that in which yellow dyeings on wool of 1,6,4,8-diaminonaphthalenedisulfonic acid became brown rapidly on insolation.³ The mono-nitro-derivatives of α - and β -naphthalenesulfonic acid are equally sensitive, but 2,4,8-dinitronaphthalenesulfonic acid is fast to light. Since, however, 1,8-nitronaphthalenesulfonic acid is highly sensitive, although the 1,5- compound is not, and since the 1,6- and 1,7- compounds are nearly equally sensitive, the degree of sensitiveness appears to be related to the positions of the nitro- and sulfonic acid groups in the nucleus.

The nitrosulfonic acids are said also to be sensitized to light by the addition of aromatic amines, due to oxidation of the amines by the nitro- group. The corresponding sulfinic acids and sulfonamides also give light-sensitive dyeings.

In the benzene series,⁴ the sensitiveness to light decreases in the order ortho, para and meta, while the sensitiveness of *o*-nitrobenzenesulfonic acid is equal to that of *o*-nitrobenzenedisulfide, although considerably less than that of 1,8-nitronaphthalenesulfonic acid. It was suggested that the sensitiveness to light is imparted by the sulfur molecule rather than by the sulfonic group as a whole. The sensitiveness of 1,2-nitronaphthalenesulphonic acid and its salts is but little less than that of the 1,8-compound. Substitution of the hydrogen atom in the sulfonic acid group does not affect the photochemical properties of the nitrosulfonic acids, but the close proximity of the nitro- and sulfonic acid groups in the same ring has a positive influence on it. The dark precipitate formed by irradiation of the 1,8-compound is probably 1-amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol, or

¹ de Laszlo, H. G., *Compt. rend.*, **180**, 203 (1925); *Z. physik. Chem.*, **118**, 369 (1925); *Proc. Roy. Soc.*, **111A**, 355 (1926). See also Charlampowiczowna, B., and Marchlewski, L., *Bull. intern. acad. Polonaise.*, **A**, 376 (1930); Obreimov, I., and Prichotjko, A., *Physik. Z. Sowj.*, **1**, 203 (1932); Kumura, S., *Mem. Coll. Sci. Kyoto Imp. Univ.*, **14**, 303 (1931); *Chem. Abs.*, **26**, 1516 (1932).

² Kemula, W., and Duncz, B. L., *Z. physik. Chem.*, **A181**, 359 (1938).

³ Vorozhtzov, N. N., and Gribov, K. A., *J. Gen. Chem. (U.S.S.R.)*, **2**, 929 (1932), *Chem. Abs.*, **27**, 2440 (1933).

⁴ Vorozhtzov, N. N., and Kozlov, V. V., *J. Gen. Chem. (U.S.S.R.)*, **2**, 939 (1932), **7**, 996, 1610 (1937); *Chem. Abs.*, **27**, 2440 (1933), **31**, 5349, 8528 (1937); *Org. Chem. Ind. (U.S.S.R.)*, **4**, 399 (1937).

an isomer containing another hydroxyl group and an NO instead of an NO₂ group. When the magnesium salt of 1,8-nitronaphthalenesulfonic acid is exposed to sunlight, the dark precipitate is probably the cyclic magnesium salt of 2-hydroxy-1,1'-azonaphthalene-8,8'-disulfonic acid.

The change occurs better on wool than on silk or cotton, but it can also be observed in aqueous solutions of the salts, especially the magnesium salt. The reaction is faster in neutral or alkaline than in acid solutions. It is hindered by oxidants. When the substituents are in the "quinogenic" (1,5 and 1,7) positions, the acid is less sensitive than when they are in the 1,6 and 1,8 positions. When paper soaked in these solutions and exposed to light is rinsed with dilute sodium bichromate solutions, the colors are set better than if pure water is used. Nitroanthracene-1-sulfonic acid forms a dark compound when exposed to light, but *meso*-nitro-anthracene-2-sulfonic acid gives a colorless compound.

Steiger⁵ studied a number of these compounds, as well as some containing the nitro-group and, in place of or in addition to the sulfonic acid group, the methyl group. The 1,8-nitromethylnaphthalene is more sensitive than *o*-nitrotoluene and nitronaphthalene. Its 5-sulfonic acid also is extremely sensitive. Pyridinium 1-nitronaphthalene-8-sulfonate and the corresponding N-methylpyridinium salt, like potassium 1-nitronaphthalene-8-sulfonate, are also very sensitive. Compounds of the series 5,1,8-C₁₀H₅(NO₂)SO₂X with a substituent in position 5 are more sensitive than those without it. The sensitivity varies with the group X and with the solvent employed.

Data for the absorption of twenty substituted 1,2- and 1,4-naphthaquinones have been given by Beck, MacBeth and Winzor.⁶ These observations played a part in the determination of the structures of two dyes, droserone and hydroxydroserone, derived from the insectivorous plant, *Drosera whittakeri*.

The substituted naphthoquinone, 2-methyl-1,4-naphthaquinone, gradually loses its color in sunlight.⁷ After two months, ether removed a colorless irradiation product, melting at 235°C. It is a dimer formed by 3,4-addition of two molecules of the naphthaquinone and contains a cyclobutane ring. That the quinone carbonyl groups did not function in the dimerization was shown by the formation of a tetraoxime of the dimer. These observations were made in the course of an investigation of the structure of the pigment phthiocol of the tubercle bacillus.

Dilute aqueous solutions of 2-hydroxy-1,4-naphthaquinone at 70°C. on exposure to ultraviolet light give isonaphthazarin and mainly, 3,3'-dihydroxy-2,2'-dinaphthyl-1,4,1',4'-diquinone.⁸

When the reaction product of 3-chloro- or 3-bromo 1,2-naphthoquinone and 2,3-dimethylbutadiene in chloroform is heated at 100°C. in sunlight, the red solution becomes yellow in about 45 minutes, then changes to red and finally becomes yellow again. After five hours there results 36 per cent of 2,3-dimethyl 1,4,11,12-tetrahydropheanthrenequinone-11,12-*endo*-2',3'-dimethyl-2'-butene. In the dark, 16 to 20 hours of heating would be required. The product is a brilliant yellow, changing to nearly colorless on exposure to the light.⁹

An acid formed by the action of alkali and red mercuric oxide on 4-methyl- β -naphthopyrone followed by treatment with hydrochloric acid, when dissolved in

⁵ Steiger, R. E., *Helv. Chim. Acta*, **16**, 793, 1315 (1933); **17**, 701, 1354 (1934).

⁶ Beck, A. B., MacBeth, A. K., and Winzor, F. L., *Australian J. Exptl. Biol. Med. Sci.*, **12**, 203 (1934); *J. Chem. Soc.*, 325, 334 (1935).

⁷ Madinaveitia, J., *Rev. acad. cienc. Madrid*, **31**, 617 (1934); *Chem. Abs.*, **29**, 5138 (1935); *Anales soc. espan. fis. quim.*, **31**, 750 (1933); *Chem. Abs.*, **28**, 1036 (1934).

⁸ Hooker, S. C., *J. Am. Chem. Soc.*, **58**, 1212 (1936).

⁹ Fieser, L. F., and Dunn, J. T., *J. Am. Chem. Soc.*, **59**, 1021 (1937).

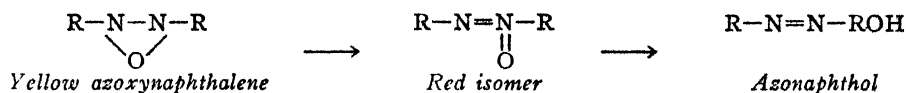
chloroform, is converted into 4-methyl- β -naphthopyrone to the extent of 70 per cent by the action of ultraviolet rays. On the other hand, a modification of the original acid, which melts at 146°C. rather than 112°C. and which is regarded as having the *cis* configuration, is unaltered when similarly treated.¹⁰ It is suggested that the *trans* form is converted into the *cis* form during irradiation. The molecules of the latter may, however, be activated in such manner that the transformation does not stop at this stage, but proceeds further until cyclization to the stable coumarin-type of molecule has been effected. On the other hand, irradiation does not appear capable of activating the molecules of the *cis* form to the extent necessary for formation of the pyrone.

Aqueous solutions of sodium naphthionate undergo a change in surface tension in light. By placing a drop of the liquid in a horizontal capillary tube and exposing one meniscus to light from a mercury arc, Grumbach and Schlivitch¹¹ estimated the increase in surface tension by the speed of motion toward the lighted end. It is of the order of 1 to 2 mm. per hour. Aqueous solutions of fluorescein, sulfofluorene and uranyl nitrate, xylene solutions of anthracene and alcoholic solutions of xylene and gasoline behave in a similar manner but solutions of ferric chloride or oxalic acid do not.

The ammonium salt of α -nitrosonaphthylhydroxylamine reddens when applied to filter paper and exposed to the rays from a quartz mercury-vapor lamp. Rays of wave-lengths transmitted through glass are effective in producing this change.¹²

β,β -Azoxynaphthalene, which has a pure yellow color and melts at 164°C. on exposure to light (preferably in alcoholic solution) is converted irreversibly into a red isomer melting at 162°C. Both forms are stable toward alcohol in the dark.¹³ The α,α' -azoxynaphthalene undergoes a change to a red form¹⁴ regarded as a hydroxyazonaphthalene. Despite the fact that attempts to characterize the red modification as such by benzylation or methylation failed, support for this structure is afforded by a comparison of the absorption spectra of both forms with that of β -naphthaleneazo- β -naphthol.

Cumming and Steel,¹⁵ however, note that exposure of the α,α' -azoxynaphthalene to sunlight or to the light of a mercury-vapor lamp for a short period produced a red isomer of the same melting point. Further exposure produced an azonaphthol, melting at 224°. This change they formulate:



1,2,7,8-Di-(1',5'-tetrazolo)-4-methyl-(1,8-naphthyridine, 1,2,7,8-tetrahydride), a light yellow material, becomes brown in a few days in air and light.¹⁶

Exposure to light converts β -2-hydroxy-1-naphthylcrotonic acid completely into 4-methyl- β -naphthopyrone, if sufficiently prolonged. β -Dimethylcoumaric acid yields 4,7-dimethylcoumarin.¹⁷

¹⁰ Dey, B. B., and Lakshminarayanan, A. K., *J. Indian Chem. Soc.*, **11**, 373 (1934); *Chem. Abs.*, **28**, 6145 (1934).

¹¹ Grumbach, A., and Schlivitch, S., *Compt. rend.*, **181**, 241 (1925).

¹² Baudisch, O., and Fürst, R., *Ber.*, **45**, 3426 (1912).

¹³ Cumming, W. M., and Ferrier, G. S., *J. Chem. Soc.*, **125**, 1108 (1924).

¹⁴ Baudisch, O., and Fürst, R., *Ber.*, **45**, 3426 (1912).

¹⁵ Cumming, W. M., and Steel, J. K., *J. Chem. Soc.*, **123**, 2465 (1923).

¹⁶ Seide, O., *Ber.*, **59B**, 2465 (1926).

¹⁷ Murty, K. S., Rao, P. S., and Seshadri, T. R., *Proc. Indian Acad. Sci.*, **6A**, 316 (1937); *Chem. Abs.*, **32**, 3362 (1938).

ANTHRACENE

This hydrocarbon differs from naphthalene in exhibiting an interesting polymerization reaction. Anthracene exhibits strong absorption bands at 3800, 3600, 3400 and 3260 Å.¹⁸ Bands were also found at 4450 and 4750 Å by Taylor and Lewis,¹⁹ who believed absorption in these bands to be responsible for the occurrence of the polymerization reaction. Subsequently, however, it was shown that the latter two bands are due to the presence of chrysogen as an impurity.²⁰ Capper and Marsh observed that pure white anthracene fluoresces with a violet-blue color, and that the addition of a trace of chrysogen changes this to the familiar magnificent green glow observed in most samples. For this reason, to excite the true fluorescence of anthracene the exciting light would have to be shorter than 4100 Å. They believed the light effective in polymerization must lie between the first absorption band at 3750 Å and 3100 Å since the reaction can be carried out in glass. Castille²¹ finds anthracene to exhibit ten bands between 3800 and 2850 Å and two more in the extreme ultraviolet.²²

The formation of an insoluble white precipitate when anthracene is irradiated in benzene solution and the recognition that it is dianthracene were subjects of early observations by Fritzsche,²³ Elbs,²⁴ and Orndorff and Cameron.²⁵ In darkness the polymer yields anthracene by a thermal reaction which goes practically to completion. The process has been employed as a means for the purification of anthracene.²⁶ A solution of crude anthracene in benzene, toluene or coal-tar naphtha is irradiated by ultraviolet rays, the dianthracene separating and leaving carbazole, phenanthrene and most of the other compounds originally present as impurities in solution. The dianthracene is filtered off and reconverted into anthracene by sublimation, yielding a product of purity of 95 per cent or higher. The method has also been employed for the removal of anthracene from such materials as phenanthrene and fluorene in which it is a contaminant.²⁷

The photostationary states set up between the polymerizing photochemical and the depolymerizing thermal reactions in phenetole, anisole and xylene solutions were studied by Luther and Weigert.²⁸ This is an instance of a photostationary state between two reactions one of which is purely photochemical and the other purely thermal. The depolymerization follows a unimolecular course, is unaffected by light, and has a temperature coefficient of 2.8. The temperature coefficient of the polymerization is only slightly greater than unity. Recently, Lauer and Oda²⁹

¹⁸ Hyatt, J. M., *Phys. Rev.*, **19**, 391 (1922).

¹⁹ Taylor, H. A., and Lewis, W. C. M., *J. Am. Chem. Soc.*, **46**, 1606 (1924).

²⁰ Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47**, 2847 (1925).

²¹ Castille, A., *Bull. acad. roy. med. Belg.*, **8**, 74 (1928); see also Shishlovskii, A. A., *Compt. rend. acad. sci. U.R.S.S.*, **15**, 29 (1937); *Chem. Abs.*, **31**, 6110 (1937).

²² For further data on various derivatives, see Barnett, E., Cook, J. W., and Ellison, T. E., *J. Chem. Soc.*, 885 (1928); Pestemer, M., and Cecelsky, J., *Monatsh.*, **59**, 113 (1932); Clar, E., *Ber.*, **65B**, 503 (1932), **66B**, 202 (1933); Lauer, K., and Oda, R., *Ber.*, **69B**, 137 (1936); Haack, E., *Ber.*, **62B**, 1771 (1929); Barnett, E., Cook, J. W., and Matthews, M. A., *Ber.*, **60**, 2353 (1927); Clar, E., *Ber.*, **62B**, 350 (1929); **63B**, 112 (1930); Clar, E., and Guzzi, A., *Ber.*, **65B**, 1521 (1932); Fieser, L. F., and Hershberg, E. B., *J. Am. Chem. Soc.*, **57**, 1681 (1935); Obreimov, I., and Prichotjko, A., *Physik. Z. Sowj.*, **1**, 203 (1932).

²³ Fritzsche, J., *prakt. Chem.*, **101**, 337 (1866).

²⁴ Elbs, K., *J. prakt. Chem.*, **44**, 467 (1891).

²⁵ Orndorff, W. R., and Cameron, F. K., *Am. Chem. J.*, **17**, 658 (1893).

²⁶ Downs, C. R., U. S. P. 1,303,639, May 13, 1919; *Chem. Abs.*, **13**, 1862 (1919).

²⁷ Capper, N. S., and Marsh, J. K., *J. Chem. Soc.*, 724 (1926).

²⁸ Luther, R., and Weigert, F., *Sitzb. Akad. Wiss. Berlin*, 828 (1904); *J. Chem. Soc.*, **86**, ii 463 (1904); *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905).

²⁹ Lauer, K., and Oda, R., *Ber.*, **69B**, 137 (1936).

found the polymerization rate to be the same in hexane, cyclohexane, cyclohexene and ethanol. It is considerably greater in acetic acid and, particularly, in benzene. This is attributed to an effect of these solvents in displacing the absorption spectrum of anthracene toward longer wave-lengths. Double bonds in the solvent molecules have a distinct accelerating effect on the reaction. The results in cyclohexene were somewhat uncertain because of a darkening of the solvent. It was also found by Luther and Weigert that in solutions in which absorption was complete a further increase of anthracene concentration tended to increase the rate of polymerization, the rates approaching a limit at higher concentrations. Various early fruitless attempts were made to account for this.³⁰

Recently, Weigert³¹ verified the dependence of the rate upon concentrations in excess of those at which absorption is complete. He employed the lines 3660 and 3130A of the mercury arc. At very low concentrations, below 0.005 per cent, the yield was approximately proportional to the concentration. At higher ones, the rate increased with concentration approaching asymptotically a maximum at about 2 per cent concentration. Between 87° and 137°C., no influence of temperature or solvent was observed. The quantum yields were 0.254 at 3660A and 0.228 at 3130A.

Weigert proposed a more elaborate mechanism for the polymerization than that of Bodenstein who merely assumed that an activated anthracene molecule on collision with a normal one formed the polymer. Weigert assumed that an activated molecule on collision may utilize its activation energy in opening the bond between the two central carbon atoms forming a diradical with two tervalent carbon atoms. Two of these can then unite to produce the polymer.

There is the possibility that this mechanism is unnecessarily elaborate and that the diradical may be directly produced as a result of absorption. Clar³² suggested that the origin of certain absorption bands is referable to the production of unpaired electrons at the meso- positions. Schönberg³³ assumes a photoequilibrium between the normal and the diradical forms of certain anthracenes, which cannot be magnetically detected because of the small concentration of the diradical form.

When anthracene is irradiated with short wave-lengths (1800 to 2000A), it exhibits a photoelectric effect.³⁴ At the same time there occurs a surface formation of dianthracene on the crystals. This Suzuki and Volmer³⁵ regard as an effect secondary to the internal photoelectric effect. They find it possible to prevent its formation by placing metal foils on both sides of the irradiated face and applying a field of 2000-14000 volts per cm.

Behavior of Various Anthracene Derivatives. Polymerization of β -methyl anthracene is a photochemical reaction similar to that of anthracene.³⁶ 2-3-Benz-anthracene in xylene is readily oxidized by air to the quinone with the aid of ultraviolet light.³⁷ The oxidation of dihydrobenzanthrone is markedly accelerated by light.

³⁰ Weigert, F., *Z. physik. Chem.*, **63**, 458 (1908); Byk, A., *Ibid.*, **62**, 454 (1908).

³¹ Weigert, F., *Naturwiss.*, **15**, 124 (1927).

³² Clar, E., *Ber.*, **65B**, 503 (1932).

³³ Schönberg, A., *Trans. Faraday Soc.*, **32**, 514 (1936).

³⁴ Volmer, M., and Riggert, K., *Z. physik. Chem.*, **100**, 502 (1922).

³⁵ Suzuki, M., and Volmer, M., *Naturwiss.*, **23**, 197 (1935).

³⁶ Orndorff, W. R., and McGraw, H. A., *Am. Chem. J.*, **22**, 152 (1899); Weigert, F., and Krüger, O., *Z. physik. Chem.*, **85**, 579 (1913).

³⁷ Clar, E., *Ber.*, **65B**, 503 (1932); **68B**, 2066 (1935).

ANTHRAQUINONES³⁸

Anthraquinone has five bands between 4250 and 3600A, one broad band between 3500 and 2850A and four bands between 2800 and 2300A. Methylantraquinones and their mono- chlor-, brom- and nitro- derivatives have been observed by Schaarschmidt and Kasai³⁹ to change from a yellowish-white to a brown color on exposure to a mercury arc. Various ones exhibit the following order of decreasing sensitiveness: 4-chloro-1-methylantraquinone, 2-methylantraquinone, 1-methylantraquinone, 3-chloro-2-methylantraquinone, 1-chloro-2-methylantraquinone, 1-chloro-2-bromomethylantraquinone, 1,3-dimethylantraquinone. (1,3-Dimethylbenzophenone was not appreciably affected when similarly treated.) The change, at least in the first of these, occurs in a vacuum or in nitrogen as well as when air is present. The change is therefore considered to consist in a transformation into a highly colored quinonoid modification which is not completely reconverted into the original form when rapidly crystallized from alcohol.

Eckert⁴⁰ has noted that when 2-methylantraquinone in acetic acid is exposed for a long time to sunlight with free access of air, the solution becomes increasingly turbid with formation of, chiefly, 2 anthraquinonecarboxylic acid, together with an alkali-insoluble product, which is very probably 2,2'-diantraquinonylethane. Other derivatives of 2-methylantraquinone and of 1-methylantraquinone react in the same way, although less markedly. The oxidation of the former proceeds much more slowly or not at all in other solvents such as toluene, which is itself oxidized to benzoic acid.

He also observed⁴¹ that a solution of potassium anthraquinone-1-sulfonate in hydrochloric acid (1:1) on exposure to light evolves chlorine and yields 1-chloroanthraquinone. Potassium anthraquinone-1,8-disulfonate similarly forms 1,8-dichloroanthraquinone, but the 1,5-disulfonate yields mainly the 1-chloro-5-sulfonate and only little of the 1,5-dichloroanthraquinone. Sodium anthraquinone-2,6-disulfonate affords little 2,6-dichloroanthraquinone and much sodium 2-chloroanthraquinone-6-sulfonate. Anthraquinone-2,7-disulfonic acid yields only products soluble in water. It was possible to isolate 2-chloroanthraquinone-7-sulfonic acid and an isomer. The nitroanthraquinonesulfonic acids react with greater difficulty. 5-, 8-, and 6-Chloro-1-nitroanthraquinones have been obtained from the corresponding sulfonic acids. The bromanthraquinones could not be isolated after exposing solutions of anthraquinone-1 (and -2) sulfonates in hydrobromic acid, although bromine was readily liberated. Eckert and Hampel⁴² find that 4,4'-dimethoxy-*meso*-benzbianthrone in chlorobenzene is converted by long exposure to sunlight into naphthobianthrone.

On exposure to light, 3,6'-diacetoxydiantraquinone in benzene solution is slowly changed into diacetoxy-naphthadanthrone.⁴³ A solution of 3,6'-dihydroxydiantraquinone in alcohol on exposure to light deposited crystals which on acetylation gave diacetoxy-naphthadanthrone and a little diacetoxyhelianthrone. When an acetone solution of dimethoxydianthrone is evaporated in daylight, the

³⁸ For absorption data, see, Hayashi, M., Kawasaki, K., and Nakayama, A., *J. Soc. Chem. Ind. Japan*, 36, *Suppl. binding*, 123 (1933); Asahina, Y., and Fujikawa, F., *Ber.*, 68B, 1558 (1935); Jones, D. C. R., and Mason, F. A., *J. Chem. Soc.*, 1813 (1934); Hayashi, M., and Nakayama, A., *J. Soc. Chem. Ind. Japan*, 37, *Suppl. binding* 238, 239 (1934); Marriott, G. J., and Robinson, R., *J. Chem. Soc.*, 1631 (1934); Castille, A., *Bull. acad. roy. med. Belg.*, 8, 74 (1928); Clar, E., *Ber.*, 65B, 503 (1932).

³⁹ Schaarschmidt, A., and Kasai, K., *Ber.*, 57B, 1671 (1924).

⁴⁰ Eckert, A., *Ber.*, 58B, 313 (1925).

⁴¹ Eckert, A., *Ber.*, 60B, 1691 (1927).

⁴² Eckert, A., and Hampel, J., *Ber.*, 60B, 1693 (1927).

⁴³ Perkin, A. G., and Yoda, G., *J. Chem. Soc.*, 127, 1884 (1925).

solute becomes rapidly converted into dimethoxynaphthodianthrone and dimethoxy-helianthrone.

Weber⁴⁴ observed that the resulting dyes were off-color when textiles which had been dipped in solutions of the leuco- compounds of certain halogen-containing anthraquinone and indigoid dyes were exposed to sunlight before oxidation. He regarded this as due to dehalogenation, since the color produced in each case corresponded to that of the halogen-free dye. This suggested a method for the removal of halogen from compounds of the anthraquinone series. Goldstein and Gardner⁴⁵ applied it with success in a number of cases. The effect is due to visible rather than to ultraviolet light. 1- and 2-Chloro-, 1- and 2-bromo-, and 1-chloro-4-hydroxyanthraquinone were exposed in alkaline sodium hydrosulfite solutions to a 500-watt Eastman "Floodlight" with exclusion of air. The anthrahydroquinones were then oxidized by air and the amount of dehalogenation calculated from the halogen content of the crude product. The final product from each of the halogen anthraquinones was identified as anthraquinone and that from 1-chloro-4-hydroxyanthraquinone as α -hydroxyanthraquinone. The α -halogen is much more readily removed than β -halogen, and bromine more readily than chlorine.

Anthrahydroquinol- α -carboxylic lactones in alkaline, acid or neutral solutions are sensitive to air, especially in benzene or xylene in light.⁴⁶ The 2-methyl derivative of anthrahydroquinol-1-carboxylic lactone gave chiefly with typical oxidizing agents 2,2'-dimethyl-9,9'-dihydroxyl-1,1'-dicarboxylic dilactone. Aqueous and especially alcoholic alkalis dissociate the latter with formation of an olive-green solution containing the salts of the anthraquinone and the anthrahydroquinol acids apparently in quinhydrone-like combination. Probably the primary step is a dissociation into an anthoxyl radical with univalent oxygen. Exposure in acetic acid to ultraviolet light, and heating in certain organic solvents, apparently also brings about a similar dissociation.

Much has been written in regard to the use of anthraquinone derivatives in facilitating photochemical oxidations of a wide variety of organic compounds. The anthraquinone in light acts as an oxygen carrier, the carbonyl groups being reduced to carbinols. These regenerate the anthraquinone on shaking with air. When dextrose is the oxygen acceptor, this reaction occurs also in the dark.⁴⁷ Other quinones (benzoquinone, naphthoquinone, acridone) xanthone and benzo-phenone are less effective. Anthraquinone is unable to oxidize naphthalene in acetic acid to phthalic acid.

Kreidl⁴⁸ uses as catalysts, in effecting such oxidation reactions, ring-system hydrocarbons containing at least three condensed nuclei, such as anthracene; substitution products of such hydrocarbons; substances of quinonoid type, with a ring system containing at least three condensed nuclei and of a lower state of oxidation with respect to at least one of the quinonoid carbon atoms than corresponds to anthraquinone; substitution products of such substances; or hydrogenated products of hydrocarbons with a ring system containing at least three condensed nuclei or their substitution products. Nozicka⁴⁹ effected such photochemical oxidation processes in the presence of a catalyst of the anthraquinone type in conjunction

⁴⁴ Weber, A. E., *Dyestuffs*, **33**, 1 (1933); *Am. Dyestuff Rept.*, **22**, 157 (1933); *Chem. Abs.*, **27**, 3336 (1933); *Brit. Chem. Abs.*, **1933B**, 344.

⁴⁵ Goldstein, A. E., and Gardner, J. H., *J. Am. Chem. Soc.*, **56**, 2130 (1934).

⁴⁶ Scholl, R., and Renner, F., *Ber.*, **62B**, 1278 (1929).

⁴⁷ Pfeilsticker, K., *Biochem. Z.*, **199**, 8 (1928).

⁴⁸ Kreidl, I., U. S. P. 1,971,042, Aug. 21, 1934; *Chem. Abs.*, **28**, 6066 (1934).

⁴⁹ Nozicka, F., German P. 526,195, October 27, 1929; *Chem. Abs.*, **25**, 4184 (1931).

with one or more auxiliary catalysts, such as sodium or potassium hydroxide, active carbon, inorganic gels or oxides of copper, bismuth, iron, vanadium or silver. Illustrative reactions⁵⁰ are the oxidation of toluene to benzoic acid, of paraffin oil to fatty acids, of lepidine to cinchoninic acid, etc.⁵¹

Oxidation of Anthracene. Hibberd⁵² states that anthracene exposed to daylight or to light of the Fade-Ometer (See Chapter 30) becomes yellow or brown and gives a positive reaction for anthraquinone. Dufraisse and Gérard⁵³ state that under certain conditions anthracene combines with oxygen to form a colorless,

crystalline photo-oxide of the structure $\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}$. This is stable at

ordinary temperatures, but at 120°C. decomposes explosively without evolution of oxygen. It can be titrated with potassium iodide, which reduces it to anthranol or oxanthrol, but isomerization and subsequent oxidation to other products also occur. The photo-oxide resembles oxanthrone in state of oxidation and in giving, with hydrochloric acid and hydrobromic acid, 10-chloro- and bromoanthrone, respectively. 9-Phenyl-10-iodoanthracene is irregularly photo-oxidizable. 9-Phenyl-10-carboxyanthracene and its methyl ester are also photo-oxidizable, but the carboxyl group apparently hinders the addition of oxygen. The photo-oxide of 9-phenylantracene can be obtained in only 30 per cent yield.⁵⁴

Although the 9,10-diarylanthracenes form photo-oxides that dissociate on heating, that of anthracene explodes at 120°C., and that of 9-phenylantracene decomposes at 155° with emission of about 12 per cent of oxygen.⁵⁵ 10-Methyl- and 10-ethyl-9-phenylantracene photooxides behave more like 9-phenylantracene than like the diaryl compounds, decomposing at 170° and 200° with evolution of 20 and 34 per cent of oxygen, respectively.

To determine whether the reason that anthracene photo-oxide does not liberate all its oxygen on pyrolysis while the corresponding diphenylantracene photo-oxide liberates 95 per cent of its oxygen⁵⁶ might be the greater oxidizability of hydrogen as compared with the phenyl group, Dufraisse and Priou⁵⁷ studied the *meso*-dimethoxy-photo-oxide in the expectation that the methoxyl radical would be less oxidizable than the phenyl. They found, however, that this explanation does not hold, since the compound is unstable in light, especially when in solution. It melts at 145°C., with decomposition, leaving a residue of anthraquinone. Willemart⁵⁸ found 9,10-di- α -naphthylantracene, as well as the di- β -naphthyl compound, when exposed to sunlight in the presence of air to yield photooxides. The latter heated at 180-200°C. lose oxygen and regenerate the hydrocarbons.⁵⁹

⁵⁰ French P. 702,183, Aug. 27, 1930, to Vereinigte Chemische Fabriken Kreidl Heller & Co.; *Chem. Abs.*, 25, 3919 (1931); Austrian P. 151,652, Nov. 25, 1937; *Chem. Abs.*, 32, 2029 (1938).

⁵¹ See also German P. 624,964, Feb. 1, 1936, to Kreidl, Heller & Co.; French P. 739,711, July 6, 1932; German P. 536,195, Oct. 27, 1929.

⁵² Hibbert, E., *J. Soc. Dyers Colourists*, 44, 377 (1928); *Brit. Chem. Abs.*, 1929B, 88.

⁵³ Dufraisse, C., and Gérard, M., *Compt. rend.*, 201, 428 (1935); 202, 1859 (1936). For a more detailed study of the influence of solvents on photopolymerization and photooxidation, which have as common intermediate an unstable dimer, see Dufraisse, C., and Gérard, M., *Bull. soc. chim.*, 4, 2052 (1937).

⁵⁴ Dufraisse, C., Velluz, L., and Velluz, Mme., *Compt. rend.*, 203, 327 (1936). Since phenanthrene and naphthalene structures do not form photo-oxides, this is a phenomenon different from the accelerated photo-oxidation of numerous unsaturated compounds. Dufraisse, C., and Priou, R., *Bull. soc. chim.*, 5, 611 (1938).

⁵⁵ Willemart, A., *Compt. rend.*, 203, 1372 (1936); *Bull. soc. chim.*, 4, 357 (1937).

⁵⁶ Dufraisse, C., and LeBras, J., *Bull. soc. chim.*, 4, 349 (1937); Dufraisse, C., Velluz, L., and Velluz, Mme., *Ibid.*, 4, 1260 (1937); Velluz, L., and Velluz, Mme., *Bull. soc. chim.*, 5, 192, 606, 1073 (1938); *Chem. Abs.*, 32, 3379 (1938).

⁵⁷ Dufraisse, C., and Priou, R., *Compt. rend.*, 204, 127 (1937).

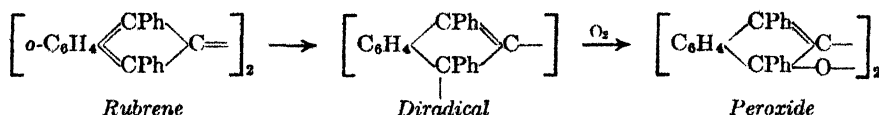
⁵⁸ Willemart, A., *Compt. rend.*, 201, 1201 (1935).

⁵⁹ See also Willemart, A., *Compt. rend.*, 202, 140 (1936); *Bull. soc. chim.*, 4, 510 (1937) for the tolyl derivatives.

9-Methyl (or ethyl)-anthracene polymerizes when irradiated. At the melting points of the polymers, the original hydrocarbons are regenerated, but under certain conditions photo-oxides may be obtained which do not evolve oxygen on heating; Dimethyl (9,10)-derivatives of 9-phenylanthracene do not polymerize.⁶⁰

Acridine and 9-phenylacridine give no light-stable photo-oxides.⁶¹

Naphthalenes. The red hydrocarbon rubrene, $C_{42}H_{28}$, (tetraphenyl rubene) forms a peroxide when its benzene solution containing dissolved oxygen is exposed to visible or ultraviolet light; no oxidation occurs in darkness.⁶² The peroxide is stable in solution, colorless and has a molecular weight of 561. Schönberg⁶³ believes light converts rubrene into an activated diradical form, which adds oxygen to form the peroxide.



The presence of hydroquinol and pyrocatechol and their methyl ethers retards the reaction. Dissociation of the peroxide into rubrene is accompanied by the emission of light. If a benzene solution of the brown form (which owes its color to the presence of an impurity and is really yellow) is exposed to sunlight and then heated to 80°C., the solution becomes luminous. Irradiation destroys the impurity, but the solution can again be activated by sunlight. When in the solid state, the yellow form is luminous after exposure to sunlight, but it is not luminous in solution.

The quantum efficiency of the formation of the peroxide of rubrene rises to unity at concentrations greater than 0.01 molar, and is independent of wave-length between 3660 and 5460 Å.⁶⁴ Bowen and Steadman believe the reaction to depend on termolecular collisions between an activated and a normal rubrene molecule and an oxygen molecule.

The mechanism of the reaction has been the subject of recent discussion.⁶⁵ Schumacher believes an excited rubrene molecule R^* incapable of forming a stable RO_2 molecule by collision with an oxygen molecule, unless it has previously collided with another R molecule to give a long-lived R^* molecule which can form a stable oxide. Another possibility, applicable to the results at low oxygen pressures, is for an R^* molecule to form with oxygen an unstable RO_2 molecule which can be stabilized by collision with another R molecule. Neither excited

⁶⁰ Willemart, A., *Compt. rend.*, **205**, 866, 993 (1937); *Bull. soc. chim.*, **5**, 556 (1938); *Chem. Abs.*, **32**, 4976 (1938). For 9-alkyl-10-phenyl-anthracenes, see *Bull. soc. chim.*, **4**, 1447 (1937).

⁶¹ Dufraisse, C., and Houpillart, J., *Bull. soc. chim.*, **5**, 626 (1938).

⁶² Moureu, C., Dufraisse, C., and Lotte, P., *Compt. rend.*, **190**, 148 (1930); Moureu, C., Dufraisse, C., and Butler, C., *Ibid.*, **183**, 101 (1926).

⁶³ Schönberg, A., *Ber.*, **67B**, 633 (1934).

⁶⁴ Bowen, E. J., and Steadman, F., *J. Chem. Soc.*, 1098 (1934).

⁶⁵ Gaffron, H., *Biochem. Z.*, **264**, 251 (1933); Schumacher, H. J., *Z. Elektrochem.*, **42**, 522 (1936); Koblitz, W., and Schumacher, H. J., *Z. physik. Chem.*, **B35**, 11 (1937); *Brit. Chem. Abs.*, **A**, **1**, 255 (1937); Gaffron, H., *Z. physik. Chem.*, **B37**, 437 (1937); *Brit. Chem. Abs.*, **A**, **1**, 40 (1938); Schumacher, H. J., *Z. physik. Chem.*, **B37**, 462 (1937).

oxygen molecules nor long-lived excited R molecules are believed to play an important part in the reaction. Gaffron found that at small concentrations the oxygen pressure affects the quantum yield. From data on the quantum yield at small oxygen pressures, he concluded that there must be, in addition to the ordinary, short-lived, active form of rubrene, another comparatively long-lived (10^{-2} to 10^{-1} second) active form during the life of which every collision leads to reaction. Schumacher has finally suggested that Gaffron may not have measured the pure rubrene oxidation. The discussion of the mechanisms, too intricate to be given here, is of some significance for the theory of photosensitized processes, since Gaffron views the oxidation, at least in the case of high rubrene concentrations, as what may be called a self-sensitized process.

The relative rates of oxidation of tetraphenylrubrene in 1:10,000 dilution in ten organic solvents in the light of a carbon arc have been determined by Dufraisse and Badoche,⁶⁶ that in benzene being taken as unity. The highest value, 9, was obtained in carbon disulfide. That in nitrobenzene was 0.10. These different rates seem to be connected with the ability of the solvents to accept oxygen. In the case of nitrobenzene, however, it is probably related to the ability of the solvent to extinguish fluorescence. The high rate observed in carbon disulfide is greatly reduced by the addition of ether. Acetone had little effect on the rate in nitrobenzene. In general, the oxidation is the more rapid the more nearly the absorption maximum in the given solvent approaches the red, but definite relations could not be deduced.

It has been suggested that pure oxygen can be extracted from air by way of the dissociable photo-oxide of rubrene or of *meso*-diphenylanthracene.⁶⁷

The compound formed by exposure of a chlorophyll solution to light in the presence of an acceptor⁶⁸ has a diradical character similar to that obtained in the case of rubrene.⁶⁹

A review of the literature on the synthesis and photochemical properties of the naphthacenes (a term used to replace rubrenes) has been given by Dufraisse and Horclois.⁷⁰ Naphthacene forms a photo-oxide, $C_{18}H_{12}O_2$, colorless needles, which gives no oxygen on decomposition. Diphenyl-9-10-naphthacene gives a photo-oxide, $C_{30}H_{20}O_2$, which liberates iodine from potassium iodide, but melts at 160° without giving oxygen. 1,2,3,4-Tetrahydro-9,10-diphenylnaphthacene gives a photo-oxide, $C_{30}H_{24}O_2$, which regenerates the original hydrocarbon and liberates 80 per cent of its oxygen at $200^\circ C$. The presence of two hydrogen atoms in the 1,1'-positions in rubrenes suppresses the reversibility of absorption of oxygen.⁷¹

1,1'-Bis(*p*-tolyl)-3,3'-diphenyl-5,5'-dimethylrubrene, $C_{48}H_{38}$, forms red solutions which are decolorized by light in the presence of air with the formation of a peroxide.⁷² Dufraisse and Loury⁷³ found ethyl-1,1'-diphenylrubrene-3,3'-dicarboxylate to form a photo-oxide which at $190^\circ C$. loses a little oxygen and much carbon dioxide. Solutions of 1,1,3'-triphenylrubrene-3-carboxylate in alcohol are moderately rapidly decolorized by sunlight, but the corresponding acid is much more

⁶⁶ Dufraisse, C., and Badoche, M., *Compt. rend.*, **200**, 1103 (1935).

⁶⁷ Dufraisse, C., and Le Bras, J., *Bull. soc. chim.*, **4**, 349 (1937).

⁶⁸ Gaffron, H., *Biochem. Z.*, **264**, 251 (1933); *Chem. Abs.*, **27**, 5763 (1933).

⁶⁹ Schönberg, A., *Annalen*, **518**, 299 (1935); Müller, E., and Müller-Rodloff, I., *Annalen*, **517**, 134 (1935); *Chem. Abs.*, **29**, 5320 (1935).

⁷⁰ Dufraisse, C., and Horclois, R., *Bull. soc. chim.*, **3**, 1872, 1880 (1936); *Brit. Chem. Abs.*, **A**, 1499 (1936).

⁷¹ Dufraisse, C., and Loury, M., *Compt. rend.*, **200**, 1673 (1935); *Chem. Abs.*, **29**, 5108 (1935).

⁷² Dufraisse, C., and Monier, J. A., Jr., *Compt. rend.*, **196**, 1327 (1933); see also Dufraisse, C., and Chovin, P., *Compt. rend.*, **197**, 1127 (1933).

⁷³ Dufraisse, C., and Loury, M., *Compt. rend.*, **199**, 957 (1934).

stable.⁷⁴ The residues from the resulting solution are complex and, when heated, evolve mainly carbon dioxide mixed with from 3.7 to 6.0 per cent of the amount of oxygen to be expected from a peroxide. In sunlight, a solution of 0.0678 gm. of 9,10,11-triphenylnaphthacene (triphenylrubrene) in 2.5 cc. of benzene absorbed one mole of oxygen in an hour and became colorless. Larger-scale work led to the isolation of the photo-oxide, $C_{36}H_{24}O_2 \cdot C_6H_6$ which, on heating under various conditions, liberated from 6 to 15 per cent of oxygen. It is probably an internal 11,12-dioxytriphenylnaphthacene.⁷⁵

Hexabromotetraphenylrubrene in benzene in direct sunlight forms colorless crystals of the peroxide, which decomposes to yield 76 per cent of the theoretical amount of oxygen at 150°C. in thirty to forty-five minutes or in fifteen minutes at 200°C.⁷⁶

OTHER HYDROCARBONS

Chrysogen, the yellow impurity occurring with anthracene, and probably a hydrocarbon, is easily destroyed by exposure of its xylene solution to light. It apparently undergoes polymerization to a colorless substance in a manner similar to anthracene.⁷⁷

In the production of skin cancers in mice by the repeated application of a 1-per cent solution of 1,2-benzopyrene in benzene, sunlight exerts an accelerating influence.⁷⁸

A benzene solution of benzaldehyde and acenaphthene, exposed to sunlight for two years, yielded⁷⁹ two polymers of benzaldehyde, one previously observed by Ciamician and Silber,⁸⁰ and the other a trimer previously obtained by Mascarelli,⁸¹ a compound corresponding to the addition of a molecule each of acenaphthene and benzaldehyde less a molecule of hydrogen. In addition, there were formed stilbene, isostilbene and resinous material.

The autoxidation of decalin is accelerated by ultraviolet, according to Castiglioni.⁸² The exposure of an alcoholic solution of 5-tetraleneacetic acid to the radiation of a quartz mercury lamp yields dihydronaphthylacetic acid.⁸³

According to Goldschmidt and Reichel,⁸⁴ the yellow product obtained together with fluorenone and $\Delta^{9,9'}$ -di-fluorenylene by the atmospheric oxidation of 9-amino-fluorene in sunlight, or ultraviolet light, can also be formed with loss of ammonia when oxygen is passed over the base at 75 to 80°C. in darkness. It must be tetrafluorenylhydrazine, its colored solutions containing the radical $(C_{13}H_9)_2N\cdot$. Optically active, colorless, 3-methoxy-9-phenylfluorene-9-thioglycolic acid turns first yellow and then orange in ultraviolet light. This change occurs also in the

⁷⁴ Badoche, M., *Compt. rend.*, **198**, 662, 1515 (1934); **200**, 750 (1935).

⁷⁵ Badoche, M., *Bull. soc. chim.*, **3**, 2040 (1936).

⁷⁶ Dufraisse, C., and Velluz, L., *Bull. soc. chim.*, **3**, 254 (1936).

⁷⁷ Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47**, 2848 (1925). For absorption data on phenanthrene see Goldschmidt, S., and Graef, F., *Ber.*, **61B**, 1858 (1928); Titeica, R., *Bul. soc. romane fiz.*, **35**, 149 (1933); *Chem. Abs.*, **28**, 1618 (1934); Clar, F., and Lombardi, L., *Ber.*, **65B**, 1411 (1932); Askew, F. A., *J. Chem. Soc.*, 509 (1935). It is not autoxidizable in light. Benrath, A., and v. Meyer, A., *Chem. Abs.*, **7**, 352 (1913).

⁷⁸ Maisin, J., and de Jonghe, A., *Compt. rend. soc. biol.*, **117**, 111 (1934).

⁷⁹ De Fazi, R., *Atti accad. Lincei*, **9**, 1004 (1929); *Chem. Abs.*, **24**, 362 (1930).

⁸⁰ Ciamician, G., and Silber, P., *Chem. Abs.*, **4**, 1619 (1910).

⁸¹ Mascarelli, L., *R. Accad. Lincei*, **15**, II, 375 (1906).

⁸² Castiglioni, A., *Gazz. chim. ital.*, **64**, 465 (1934); *Brit. Chem. Abs.*, **A**, 1184 (1934); Moureu, C., Dufraisse, C., and Chauv. R., *Chem. Abs.*, **21**, 1914 (1927). For the irradiation of squalene, see *J. Soc. Chem. Ind.*, **181** (1926).

⁸³ Schroeter, G., *Ber.*, **58**, 713 (1925).

⁸⁴ Goldschmidt, S., and Reichel, L., *Annalen*, **456**, 152 (1927).

case of solutions of phenylfluorenylcarbinols, but the 9-phenylfluorenes are insensitive to light. Racemization is the principal effect of light.⁸⁵

Crude synthetic perylene may be purified by exposing it to a quartz mercury arc.⁸⁶ Ether solutions of crude coal-tar show increased ultraviolet transmission after having been similarly irradiated.⁸⁷

On illumination of a cyclohexane solution of carotene, the pressure of oxygen above it in a closed vessel drops initially and reaches a constant value in about three hours. If all or part of the oxygen is then pumped out in the dark, on re-illumination, a pressure rise is observed, indicating an equilibrium between carotene, its oxide and oxygen. But in the case of an octane solution, the oxygen pressure decreases linearly with time without reaching a minimum value.⁸⁸

⁸⁵ Lifschitz, I., *Rec. trav. chim.*, **54**, 397 (1935); *Chem. Abs.*, **29**, 5437 (1935).

⁸⁶ Postovskii, I. Y., and Bednyagina, N. P., *J. Gen. Chem. (U. S. S. R.)*, **7**, 2929 (1937); *Chem. Abs.*, **32**, 5396 (1938).

⁸⁷ Herrick, J. F., and Sheard, C., *Proc. Soc. Exptl. Biol. Med.*, **26**, 33 (1928).

⁸⁸ Baur, E., *Helv. Chim. Acta*, **20**, 402 (1937).

Chapter 27

Compounds with Heterocyclic Rings

OXYGEN-CONTAINING RINGS

Essential Oils. The spontaneous transformation of solutions of various odorous substances into a colloidal state by exposure to light has been investigated by Zwaardemaker and Hogewind.¹ In the case of several substances the change occurred only in the presence of ultraviolet light and the resulting colloidal particles were negatively charged. Among the substances studied were eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol and hypnone.

A sample of dark yellow distilled lavender oil was found by Quilico² to be progressively decolorized by exposure to ultraviolet rays without losing its original fragrance. After one hour, 20 cc. were colorimetrically equivalent to only 19.5 cc. This became 11.5 cc. after 7, 2.5 after 14 and 0.5 cc. color equivalent after 21 hours. Eucalyptus oil was decolorized slightly more rapidly. It was suggested that the formation of oxygenized products caused the slightly lower results in the lavender oil. The essential oil of *Monarda fistulosa* behaves in the opposite manner, becoming brown when exposed to light, according to Badzynski.³

Absorption data on a series of oils have been given by Morton⁴ and may serve as an aid in the identification of constituents. Maxima are found at 3070 and 2370A (wintergreen), 2810 and 2435A (almond), 2810A (clove), 2770A (thyme), 2860A (cinnamon and cassia), 2850 and 2330A (sassafras), 3110A (lemon), 2380A (mustard), 2320A (cade). Wormseed and mace oils show but little selective absorption. Previous observations on the use of ultraviolet spectrograms in the identification of essential oils were due to Boyer.⁵

It is well known that good quality peppermint oil when used in flavoring certain candies or sugar preparations, such as ordinary mint tablets, loses its fine flavor on long standing. In the laboratory of the senior author, a number of samples of such tablets were exposed to the action of ultraviolet in order to test the stability of certain mint oils in the manufacture of confections. It was found that a few hours' exposure afforded approximately the same aging effect as standing on the shelves for a period of several months. The procedure appears to be a ready method of testing materials of this class to determine quickly their keeping qualities.

It is said that the oxidation of Russian turpentine is more rapid in sunlight

¹ Zwaardemaker, H., and Hogewind, F., *Proc. Akad. K. Wetensch. Amsterdam*, 21, 131 (1918); *J. Chem. Soc.*, 116, ii, 14 (1919).

² Quilico, A., *Rivista ital. essenze profumi*, 10, 148 (1928); *Chem. Abs.*, 23, 2784 (1929).

³ Badzynski, S., *Wiadomosci Farm.*, 60, 689 (1933); *Chem. Abs.*, 28, 1815 (1934).

⁴ Morton, R. A., *Perfumer and Essential Oil Record*, 20, 258 (1929). See also Harvey, E. H., *J. Am. Pharm. Assoc.*, 19, 1173 (1930); *Chem. Abs.*, 25, 5850 (1931); van Os, D., and Dykstra, K., *J. pharm. chim.*, 25, 437, 485 (1937).

⁵ Boyer, J., *Am. Perfumer*, 17, 389 (1922).

⁶ Korotkov, K. N., *Mem. Beloruss. State Acad. Agr.*, 5, 16 (1927); *Brit. Chem. Abs.*, B, 650 (1929); *Lesokhim. Prom.*, 4, No. 11, 6 (1935); *Chem. Abs.*, 30, 8658 (1936).

⁷ Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, 12, 93 (1915); *J. Chem. Soc.*, 108(ii), 80 (1915).

than in artificial light,⁶ due to its ultraviolet rays. Jorissen and Vollgraff⁷ claim that the autoxidation of pinene under the influence of the rays from a Uviol lamp increases the electric conductivity of oxygen.

Pinene itself on exposure to ultraviolet rays gives acetylene, ethylene and hydrogen, the liquid containing some isoprene.⁸

Dedichen and Halse⁹ expose raw turpentine oil to the action of ultraviolet rays while subjecting it to the action of air or oxygen. The oil is then treated with iron chloride to refine and deodorize it, and obtain a mixture of α - and β -pinenes containing dextrorotatory β -pinenes.

Selenious acid or anhydride may react, under pressure and in the presence of ultraviolet light, with compounds containing the group $\text{CH}=\text{CHCH}_2$, eventually yielding unsaturated α - β -diketones. As starting materials, 1-methane, α -pinene, β -pinene, dipentene-3-methene and eugenol may be employed.¹⁰

When light acts on mixtures of acetone with some terpene alcohols the formation of pinacols can be confirmed. No other derivatives could be isolated by Scagliarini and Saladini.¹¹ Terpinol hydrate did not condense with acetone. However, 79.7 gm. of acetone and 53 gm. of geraniol after thirteen months in sunlight gave 63 gm. of acetone, 32 gm. of geraniol and a yellowish residue, boiling at 208-10°C. and composed of $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\cdot\text{C}\cdot\text{CH}_3=\text{CHCH}(\text{OH})\text{C}(\text{OH})(\text{CH}_3)_2$. From a similarly exposed mixture of acetone and menthol about 90 per cent of the original compounds and an analogous condensation product were recovered. Similar results were attained with borneol and acetone.

When air is passed through isoeugenol in which is immersed a lamp emitting ultraviolet rays, vanillin is formed.¹² The rate of oxidation depends upon the penetrating power of the rays. This in turn depends upon the clearness of the isoeugenol and makes necessary the use of the more expensive distilled isoeugenol. Even with this, the oil darkens in a couple of hours and the rate of oxidation rapidly decreases. Another difficulty attending the commercial application of the process is the fact that the rapid circulation of air through the solution as employed in practice caused a considerable loss of isoeugenol by vaporization. In one run in which 30,000 cu. ft. of air were circulated per hour through 800 lbs. of isoeugenol, the loss amounted to about 80 lbs. in eight hours. It was presumed that the oxidation of the isoeugenol was due to the action of ozone formed in the circulated air by the ultraviolet rays. Genthe and Co.¹³ claim that the yield of vanillin may reach 95 per cent.

Scagliarini and Saladini¹⁴ exposed 4.7 gm. of fenchone and 4 gm. of toluene in 100 cc. of water in 5-liter flasks full of oxygen to sunlight for nearly a year. Much carbon dioxide was formed and 9.3 gm. of benzoic acid could be separated from eight such flasks in addition to some acetic acid. Similar experiments with fenchone and ethyl alcohol in water gave much carbon dioxide, considerable acetic and some oxalic acids and an undetermined compound with 49.39 per cent carbon and 11.32 per cent of hydrogen. Neither fenchone nor alcohol could be oxidized separately and no easily oxidizable addition product of the two could be detected.

⁸ Urbain, E., and Scal, C., *Compt. rend.*, 168, 887 (1919).

⁹ Dedichen, H., and Halse, O. M., U. S. P. 1,253,793, Jan. 15, 1918; *Chem. Abs.*, 12, 770 (1918).

¹⁰ Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935; French P. 751,807, Sept. 11, 1933; *Chem. Abs.*, 29, 6246 (1935).

¹¹ Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, 53, 135 (1923); *Chem. Abs.*, 17, 2281 (1923).

¹² Wood, B. G., *Chem. & Met. Eng.*, 28, 399 (1923).

¹³ Genthe and Co., German P. 224,071.

¹⁴ Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, 53, 135 (1923); *Chem. Abs.*, 17, 2281 (1923).

Similar experiments with pinene and oxalic acid gave carbon dioxide, tar, much unchanged pinene and oxalic acid and some acetic acid.¹⁵

β -Caryophyllene nitrosite in solution evolves nitrogen when exposed to red light.¹⁶ Its absorption is confined to a narrow band with its head at about 6800Å.¹⁷ The quantum yield is, for the nitrogen formed, 0.38 and for the disappearance of the nitrosite as determined optically, 1.37.¹⁸ These values were obtained with oxygen excluded. In its presence, the latter value was higher, 2.9. The gas evolved in the absence of oxygen contained 86.1 per cent nitrogen and 13.9 per cent of nitrogen trioxide.

That nitropiperonal becomes brown on exposure to sunlight was noted by Ekeley and Klemme.¹⁹ Since the isomeric nitropiperonal isolated from a Kahlbaum product is brownish-yellow, it was thought that it might have been produced from the ordinary form by a light reaction. When, however, ordinary nitropiperonal was exposed in thin layers to sunlight and to ultraviolet light, the brown product yielded on recrystallization only nitropiperonal and a tarry brown residue but no isomer.

Piperitone in aqueous acetic acid or alcohol yields (in the light of a quartz mercury arc) needles of a dimer which can be separated into three fractions of the same composition and molecular weight, but which differ in form, melting point and ability to form a semicarbazone. Carvone seems also to form two dimers under these conditions. In sunlight, however, both piperitone and carvone each form only one dimer.²⁰

Pimpinellin when subjected in a thin layer to diffused sunlight for two and a half months or to ultraviolet light for 16 hours, and then extracted with ethyl acetate, yields a dimer melting at 237-8°C. When heated four hours on a water-bath with 5-per cent sodium hydroxide this dimer gives furan-2,3-dicarboxylic acid. The action of light upon pimpinellin in cold acetic acid gives a different dimer, melting at 256-7°C., from which the furan derivative could not be isolated after alkaline treatment.²¹

Attempts to isomerize campholic acid by means of ultraviolet light have not been successful²²; nor does ultraviolet light accelerate the isomeric change of nitrocamphor, or of hydroxymethylene camphor.²³ In the case of aminomethylene camphor there is a marked acceleration, which ceases when the stimulus is removed. Benzoylcamphor also undergoes isomeric change more rapidly in the presence of radiation, but the acceleration persists after the rays have been withdrawn, possibly because of the liberation of benzoic acid which acts as a powerful catalyst in promoting the isomeric change.

In sunlight, α -naphthylaminocamphor in chloroform forms substituted green compounds with the solvent; the reactions are reversed in darkness. The substance is oxidized in solution in the presence of light, and eventually naphthylamine liberated in the reaction precipitates in the form of hydrochloride.²⁴ Singh and

¹⁵ For other early observations of this type see Ciamician, G., and Silber, P., *Atti accad. Lincei*, 22, II, 470; Suida, H., *Monatsh.*, 33, 1277 (1912); Benrath, A., and v. Meyer, A., *Chem. Abs.*, 7, 352 (1913).

¹⁶ Kremers, E., *Pharm. Arch.*, 2, 273 (1899).

¹⁷ Mitchell, S., *J. Chem. Soc.*, 3238 (1928).

¹⁸ Hoffman, R. M., *J. Am. Chem. Soc.*, 56, 1894 (1934).

¹⁹ Ekeley, J. B., and Klemme, M. S., *J. Am. Chem. Soc.*, 50, 2714 (1928).

²⁰ Treibs, W., *Ber.*, 63B, 2738 (1930); *Chem. Abs.*, 25, 1513 (1931).

²¹ Weasely, F., and Dinjasky, K., *Monatsh.*, 64, 131 (1934); *Chem. Abs.*, 28, 6435 (1934).

²² Lipp, P., and Reinartz, F., *Helv. Chim. Acta*, 10, 611 (1927).

²³ Lowry, T. M., and Courtman, H. R., *J. Chem. Soc.*, 103, 1214 (1913).

²⁴ Mitra, B. N., *J. Phys. Chem.*, 35, 2371 (1931); *Chem. Abs.*, 25, 5350 (1931).

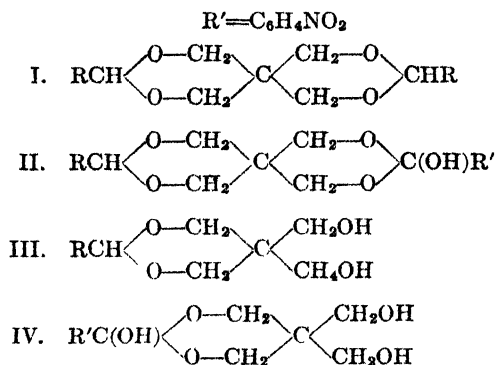
Bhaduri²⁵ extended the observations of phototropic change to other solvents. It is absent in methyl, ethyl or ethylene iodides. The oxidation reaction yields α -naphthyliminocamphor and the rotatory power is increased. Both reactions are inhibited by water or sodium ethylate.

Diazocamphor prepared from inactive camphor, as well as that prepared from the dextro-compound, are decomposed in benzene solution by light of wave-length 2200-3000A, but visible light has almost no action.²⁶

The transformation of santonin into photosantonin acid and isophotosantonin acid proceeds by way of intermediate compounds.²⁷ Photosantonin acid and probably also isophotosantonin acid are very transparent to ultraviolet rays, but santonin is not. No confirmation could be obtained by Piutti of the reported reconversion of yellow santonin into white on boiling. Any visible alteration of santonin crystals under radiation could not be confirmed.

Other Compounds with Oxygen in Rings. 3-Methylcyclohexenone irradiated by a mercury arc for seventeen hours in dilute methanol gives a saturated dimer melting at 144-5°C. and an unsaturated liquid, oily dimer. The photodimer of 3,5-dimethylcyclohexenone melts at 161-2°C. The mother liquor gives an isomer and an unsaturated substance, boiling at 203-5°C. (17 mm.).²⁸

Tănăsescu²⁹ finds that *bis-o*-nitrobenzalpentaeerythritol-1-spiran (I) in the solid state becomes slowly colored in sunlight. The change proceeds more rapidly in solution, especially in benzene. (Compare nitrobenzaldehyde.) Only one of the two nitro groups in I reacts with the formation of a compound II. By alkaline saponification of II, *o*-nitrosobenzoic acid and a product III are formed. That III still contains an unaltered nitro- group is shown by its photochemical behavior,



whereby it is rapidly converted into IV. I rapidly becomes colored on exposure in the solid state to sunshine, the melting point falling in ten days from 166° to 95°C. In ethanol, no crystallizable reaction products can be recovered, but in acetone, ethyl acetate, chloroform, pyridine, and especially benzene, the reaction product is the compound II, of melting point 135°C. In the last-named solvent, the reaction requires only fifteen minutes.

²⁵ Singh, B. K., and Bhaduri, B., *Trans. Faraday Soc.*, **27**, 478 (1931); *Chem. Abs.*, **25**, 5627 (1931).

²⁶ Bredig, G., Mangold, P., and Williams, T. G., *Z. angew. Chem.*, **36**, 456 (1923); *Chem. Abs.*, **17**, 3868 (1923).

²⁷ Piutti, A., *Atti accad. Lincei*, **22**, ii, 92 (1913).

²⁸ Treibs, W., *J. prakt. Chem.*, **138**, 299 (1933).

²⁹ Tănăsescu, I., *Bul. soc. stiinte Cluj*, **2**, 111; *Chem. Abs.*, **19**, 2932 (1925). See also Radulescu, D., *Chem. Abs.*, **18**, 1285, 1286 (1924).

³⁰ Cornubert, R., Andre, M., de Demo, M., Joly, R., Louis, P., Robinet, P., and Strehel, A., *Bull. soc. chim.*, **5**, 513 (1938); *Chem. Abs.*, **32**, 5384 (1938).

Benzylidene derivatives of α -methylcyclohexanone and α -methylcyclopentanone, and of α -isopropylcyclopentanone, undergo oxidation or polymerization on standing. This may be accelerated by ultraviolet light.⁸⁰

4-Methyl-2,6-dianisal-1-cyclohexanone is photosensitive and slowly turns orange-red behind glass. Its pale rose pentabromo-derivative is also photosensitive, turning maroon and violet-red.⁸¹

Mixtures of indole, various aldehydes and ethyl alcohol, set aside in closed bottles in diffused light for one year and then in sunlight for another year, showed progressive chromatic changes.⁸² These were greatest with α -methylindole, less evident with indole and least with scatole. This agrees with the ease of formation of rosindoles from these three compounds. Distilled with steam, the distillate contained unaltered indole, while from the filtered residue the aldehyde was recovered on cooling. In every case there was also recovered from the residue a rosindole. Solutions of diindyl-*m*-methoxy-*p*-hydroxybenzylidene in methanol, ethanol, acetone, chloroform and ethyl acetate are at first colorless, but become intense red on exposure to light and air.

Stobbe and Färber⁸³ have carried out a series of experiments on the photopolymerization of pure indene. In ultraviolet it resinified.⁸⁴

de Fazi⁸⁵ illuminated 2.5 gm. of α -methyl- β -phenylindone in 10 cc. of dry benzene in a quartz test tube with a 1500 c.p. quartz mercury arc for a total of 71 hours during 13 days. Crystals of one form of dimethyldiphenyltruxone separated, white, melting at 307-8°C. From the benzene, unchanged α -methyl- β -phenylindone and the other isomer of the dimethyldiphenyltruxone, yellow, melting at 250-260°, were separated. Each isomer treated with concentrated sulfuric acid gave α -methyl- β -phenylindone. The white isomer is sensitive to light, developing a partially reversible yellow color. In sunlight, the yellow form at the melting point for ten minutes is converted into α -methyl- β -phenylindone. The oxime and phenylhydrazone of α -methyl- β -phenylindone were exposed to ultraviolet light in benzene. A small amount of a new compound, melting at 73-5°C., was obtained, but the oxime and phenylhydrazone of dimethyldiphenyltruxone have not been obtained in this way. From β -phenyl- β' -phenyltruxone irradiated in benzene with ultraviolet for 48 hours a new yellow isomer of β -phenyl- β' -phenyltruxone, melting at 184-5°, was obtained.⁸⁶

The reciprocal reduction and oxidation of ketones and alcohols by light to pinacols and aldehydes occurs also in the case of α,β' -diisoxazole ketone.⁸⁷ Ten grams of this compound and 70 cc. of 95-per cent ethanol in a sealed tube exposed to sunlight until the reaction was complete (ten days) yielded 9.7 gm. of α,β' -diisoxazolepinacol, melting 195-6°C. Exposure of the ketone in benzene and in toluene to sunlight led only to traces of reduction products and to unidentified tars. In water, the reaction was very slow, the corresponding acid being formed after six months.

⁸¹ Poggi, R., and Gottlieb, M., *Gazz. chim. ital.*, **64**, 852 (1934); *Chem. Abs.*, **29**, 2152 (1935).

⁸² Mingoia, Q., *Gazz. chim. ital.*, **56**, 781 (1926); *Chem. Abs.*, **21**, 1118 (1927).

⁸³ Stobbe, H., and Färber, E., *Ber.*, **57**, 1843 (1924).

⁸⁴ Gunz, A., and Minguin, J., *Compt. rend.*, **152**, 373 (1911); note Weger, M., and Billmann, A., *Ber.*, **36**, 642 (1903); Ciamician, G., and Silber, P., *Ber.*, **46**, 420 (1913).

⁸⁵ de Fazi, R., *Gazz. chim. ital.*, **54**, 996 (1924). Dichlorohydrindones from the chlorination of α -methyl- β -phenylindone slowly lose chlorine in diffused light. De Fazi, R., and Pirrone, F., *Gazz. chim. ital.*, **67**, 128 (1937); *Chem. Abs.*, **31**, 6649 (1937).

⁸⁶ See also Stobbe, H., and Zschoch, F., *Ber.*, **60B**, 457 (1927).

⁸⁷ Freri, M., *Gazz. chim. ital.*, **63**, 419 (1933); *Chem. Abs.*, **27**, 5327 (1933).

⁸⁸ Milas, N., and McAlevy, A., *J. Am. Chem. Soc.*, **56**, 1219 (1934).

Ultraviolet light of wave-lengths in the range 4500 to 3600A accelerates considerably the decomposition of furoperacid (obtained from di-furoyl peroxide) either in the solid state or in solution in glacial acetic acid.³⁸

COMPOUNDS CONTAINING NITROGEN

The lower melting form (65.5-66.5°C.) of methyl-4-benzylidene-3-methylhydantoin-1-acetate when exposed to daylight or ultraviolet light in the presence of a trace of iodine is partly converted into the stereoisomer melting at 98.5-99.5°C. and partly into a polymer melting at 276-278°C.³⁹

Some decomposition also occurs with formation of benzaldehyde. The higher-melting stereoisomer similarly yields the lower-melting form and the polymer, the change being preceded by an induction period. 4-Benzylidene-3-methylhydantoin-1-acetic acid also exists in two stereoisomeric forms, melting at 186.5-187.5° and 198.5-199.5°C. The former does not yield measurable quantities of other products when exposed to light for five months. The latter is much more rapidly changed, with production of a small proportion of the lower-melting form and a polymer melting at 293-294°C.

Thymine glycol is easily broken down even in neutral solution by daylight or light from a carbon arc. Lactic aldehyde is formed as an intermediate product which isomerizes into acetol. In weakly alkaline solution, thymine glycol yields urea, acetol and carbon dioxide. In the presence of an oxidizing agent, the products are urea, pyruvic acid and carbon dioxide. With hydrochloric acid solutions or in solutions in which the acidity is produced by the growth of sulfur bacteria, a new anhydride of thymine glycol is produced by carbon arc irradiation. A deep red compound which forms in acid thymine glycol solutions is decolorized upon irradiation to a faint yellow, which shows a green fluorescence in ultraviolet light.^{40, 41}

3-Methyl-6,7-benzoylene- β,β -benzopyrrole readily forms solvates and its solutions show different colors which are more or less rapidly decolorized by light, especially ultraviolet light.⁴²

α -Picoline in benzene in the presence of anthraquinone gave, after five months of exposure to sunlight, 5.3 per cent of picolinic acid and about 10 per cent of a dark resinous substance soluble in normal sodium carbonate, difficultly soluble in twice normal hydrochloric acid, and giving no precipitate in alcohol with picric acid. Of the anthraquinone, 97.5 per cent was recovered unchanged in experiments of John and Behmel.⁴³

Pyridine. Freytag and Neudert find,⁴⁴ contrary to Berthelot and Gaudechon, that pyridine is changed by ultraviolet radiations of wave-length less than 3000A. The change is marked by a strong yellow color and an increase in density from 0.97827 to 0.98232 in less than five hours. In methyl alcohol a yellow color begins to appear after four minutes and is marked after two hours. In ethyl alcohol it is first seen in five to ten minutes, in acetone in ten minutes, in amyl alcohol in three minutes and in benzene in thirty minutes. Various salts accelerate the appearance

³⁸ Hahn, D. A., and Evans, J., *J. Am. Chem. Soc.*, **49**, 2877 (1927).

³⁹ Johnson, T. B., Baudisch, O., and Hoffmann, A., *J. Am. Chem. Soc.*, **54**, 1106 (1932); Bass, L. J., *Ibid.*, **46**, 190 (1924) has discussed the oxidation of thymine in light. See also Baudisch, O., and Davidson, D., *Ber.*, **58B**, 1680 (1925).

⁴¹ For the photosensitivity of various pyrrole ferrocyanides, see Pratesi, P., *Gazz. chim. ital.*, **65**, 658 (1935).

⁴² Scholl, R., Böttger, O., and Stix, E., *Ber.*, **67B**, 1922 (1934).

⁴³ John, H., and Behmel, G., *Ber.*, **66B**, 426 (1933); *Chem. Abs.*, **27**, 3216 (1933).

⁴⁴ Freytag, H., and Neudert, W., *J. prakt. Chem.*, **135**, 15 (1932); *Chem. Abs.*, **27**, 724 (1933). Freytag has reviewed his extensive investigations, *Phot. Korrr.*, **73**, 17, 37, 57 (1937).

of the color and others inhibit it. Inorganic and organic acids also catalyze the reaction, hydrochloric, nitric, malic and citric acids being particularly effective. Bases are inactive. The zinc chloride compound of pyridine is decomposed into its constituents and the pyridine is changed into the colored photopyridine.

Filter paper impregnated with pyridine, its hydrate or alcoholate, is colored yellow by ultraviolet light. Such papers give various colors on the addition of the salts of aromatic amines. Thus α -naphthylamine hydrochloride gives a light brownish-yellow color and the β -isomer a carmine red color. By the use of such papers, aniline hydrochloride may be detected in dilutions of one part in ten thousand. The test may also be adapted to the detection of pyridine in a dilution of 1:26,840. Since the photopyridine is sensitive to water, the test papers should be protected from moisture. Although the color reactions of irradiated pyridine with primary amines are not in every case sufficiently definite to identify the amine, they may serve to indicate the class to which it belongs.⁴⁵ The color and fluorescence of solutions of photopyridine with each of 21 aromatic sulfonic acids were also given. F-acid does not react, probably because of the hindering effect of the sulfonic acid group in position 7. The colors produced in most of these identification tests are changed to yellow or orange by alkalis, but the original color is restored by acids.

"Photopyridine" can be isolated by treating the pyridine solution with zinc chloride. It is obtained as a syrup, ruby-red in color, which decomposes on heating and evolves the odor of pyridine. With boiling β -naphthylamine hydrochloride, it gives red-brown needles, which yield colorless crystals on heating. *p*-Nitroaniline hydrochloride gives an orange color; the ether solution is reddish orange, with a green fluorescence. "Photopyridine" is not formed in the absence of oxygen, but it is not among the products of reaction of pyridine with ozone or hydrogen peroxide. It gives a violet color with a purple-violet fluorescence with sodium, potassium and calcium hydroxides, but not with sodium carbonate, sodium borate, disodium phosphate or ammonia. It gives aldehyde reactions and evolves ammonia on treatment with alkalis, and may be regarded as the ammonium derivative of the enolic form of glutacondialdehyde, $\text{CHO} \cdot (\text{CH}=\text{CH})_2\text{ONH}_4$.⁴⁶

"Photopyridine" is formed by wave-lengths in the region 2540 to 2660Å.⁴⁷ Various derivatives of pyridine are also affected by the lines 2540 and 2650 and to a smaller extent by 2480 and 2400Å.⁴⁸ With the exception of *sym*-collidine, the photoproducts of the homologous pyridines are similar to photopyridine in structure. These include 2-, 3- and 4-methyl, 2,4- and 2,6-dimethyl, 2,4,6-trimethyl, 2,3,4,5-tetracarboxyl and 2-aminopyridines. The 3-amino- derivative is most affected at the wave-lengths 3650, 3130 and 3020Å. The resulting photoproducts of these pyridines may be identified by the colors they give with β -naphthylamine. The derivative from diethyl collidinedicarboxylate is apparently the same as that from its hydrogen derivative. The photoproducts are in most cases destroyed by diffused or direct sunlight. Certain pyridines irradiated by wave-lengths less than 3000Å become yellow to yellow-brown in aqueous or alcoholic solutions although the products may not be aldehydic, the enol-aldehyde being converted into the dialdehyde form which is then resinified by free acid.

⁴⁵ Freytag, H., *J. prakt. Chem.*, **139**, 44 (1933); *Chem. Abs.*, **28**, 1701 (1934); *J. prakt. Chem.*, **136**, 193 (1933); *Chem. Abs.*, **27**, 2449 (1933).

⁴⁶ Feigl, F., and Anger, V., *J. prakt. Chem.*, **139**, 180, 343 (1934); Freytag, H., *Ber.*, **67B**, 1995 (1934); **69B**, 32 (1935).

⁴⁷ Freytag, H., and Hlučka, F., *J. prakt. Chem.*, **136**, 288 (1933); *Chem. Abs.*, **27**, 2687 (1933).

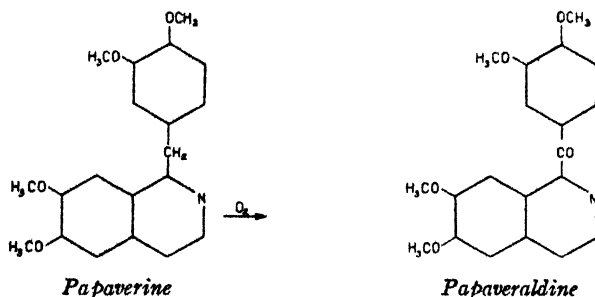
⁴⁸ Freytag, H., *J. prakt. Chem.*, **138**, 264 (1933); *Brit. Chem. Abs.* **1933A**, 1304; *Ber.* **69B**, 32 (1936); *Chem. Abs.*, **30**, 2966 (1936).

A solution of 3-bromo-5-aminopyridine, which assumed an intense color in a short time, gave no aldehyde reactions, but increased in acidity during the first hour and showed the presence of bromide ions. The increasing color possibly acted as an internal filter and slowed the reaction. Oxygen was involved since the coloration began at the surface. The amino- group also may possibly have been attacked. 2-Methyl-5-aminopyridine becomes yellowish-brown but gives no aldehyde reactions and shows no change in pH. Another group of derivatives shows no coloration, but if they contain halogen atoms or esterified carboxyl groups may form halogen ions or free acids on irradiation. Stable toward ultraviolet are 4-chloropicolinic acid and 5-aminopyridine-3-carboxylic acid, which latter has a magnificent blue-violet fluorescence, as well as pyridine-2,3-dicarboxylic acid and coramine, $3\text{-C}_6\text{H}_4\text{NCON}(\text{C}_2\text{H}_5)_2$. The chlorine atom is not removed from 4-chloro-2-aminopyridine which becomes colored, possibly because the amino- group is attacked. The rapid brown-yellow coloration of aqueous solutions of 5,6-dichloropyridine-3-aldehyde and the 4,6,2-isomer may be due to attack of the aldehyde group. 4-Iodopyridine-2-carboxylic acid in acid solution liberates hydriodic acid, which is photo-oxidized to iodine and water. Photochemical saponification of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate occurs.

Pure, colorless 2-benzylpyridine, on standing in diffused daylight, becomes yellow-red to brown and shows weak green fluorescence.⁴⁹ Filter paper impregnated with a solution of the base (two drops in 10 cc. of alcohol or benzene) turns yellow or brown after one-half to one minute in daylight, gray-brown or greenish after one hour. The product gives a red-purple dye with hot β -naphthylamine solution. With this pyridine derivative, the color of the photoproduct differs somewhat with the wave-lengths used for the irradiation. Longer ones (3650-2700Å) give a green discoloration and shorter ones (2650-2480Å) a yellow one. The shorter rays produce the usual aldehydic substance and the longer ones, 2-benzoylpyridine with α,β -diphenyl-di-2-pyridylethane.⁵⁰

The reaction has been used in printing fabrics.⁵¹ The fabric is impregnated with a solution of 2-benzylpyridine in 96 per cent alcohol; after evaporation of the alcohol the fabric is covered with a negative plate and exposed to sunlight or ultraviolet rays. When working on cotton, the positive is washed with soap, rinsed and ironed while still moist.

Müller and Dorfman find both pyridine and papaverine, in oxygen-free



⁴⁹ Freytag, H., and Müller, A., *Naturwiss.*, **21**, 720 (1933); *Chem. Abs.*, **28**, 710 (1934).

⁵⁰ Müller, A., and Dorfman, M., *J. Am. Chem. Soc.*, **56**, 2787 (1934); *Monatsh.*, **65**, 411 (1935).

⁵¹ Freytag, H., and Müller, A., *Monatsschr. Textilind.*, **48**, 239 (1933); *Chem. Abs.*, **28**, 5245 (1934).

water vapor, to be unaffected by light,⁵² but 2-benzylpyridine, 2-benzoylpyridine and papaveraldine darken. Papaverine in benzene gives 10 per cent of papaveraldine. In the solid state and in presence of oxygen, papaverine and papaveraldine become brown after several hours in mercury light.

Koller⁵³ states that 6-styryl-2,4-dichloro-3-cyanopyridine (obtained by heating the 6-methyl compound with benzaldehyde) changes in diffused daylight into a substance melting considerably higher and of double the molecular weight of the original compound. That the polymerization consists in the formation of a cyclobutane ring, with destruction of the ethylene bonds of two molecules of the styryl compound, is indicated by the fact that although the original compound is yellow, the polymer is colorless. The polymer does not react with potassium permanganate in cold acetone. Thinking this polymerization might be a property of stilbazoles in general, Koller exposed a number of other compounds of this type to sunlight and to quartz light but was in no case able to effect dimerization. Cantieni⁵⁴ finds that, in the presence of 0.001 to 1 per cent of pyridine, there is evolution of carbon monoxide from fructose solutions when exposed to ultraviolet light. The solution also turns brown. More concentrated pyridine solutions did not produce this effect, which is proposed as the basis of a method for the detection of pyridine in very dilute solutions containing not less than 0.001 per cent. Acetone inhibits the formation of the color, which is less readily formed in solutions containing glucose, galactose, sucrose or lactose. Pure pyridine and aqueous solutions more concentrated than 1 per cent are opaque, and solutions more dilute than 0.001 per cent are transparent to ultraviolet light.

Filter paper soaked in an alcoholic solution of quinoline or lepidine, treated with a 0.05 per cent aqueous solution of pyridine and irradiated, slowly becomes yellow. The reaction may be used for the detection of pyridine in the presence of nicotine, since the latter gives only a grayish color.⁵⁵

Phototropy is exhibited by 2,4,4,6-tetraphenyl-1,4-dihydropyridine, as well as by diphenacyldiphenylmethane, 2,4,4,6-tetraphenyl-3,5-dibenzoyl-tetrahydropyran, all three becoming violet in light and reverting to colorless in the dark.⁵⁶

2-Phenyl-3-methyl-quinoline in benzene solution in the presence of anthraquinone gives (on prolonged exposure to sunlight) in addition to dark resinous matter about 3 per cent of 2-phenylquinoline-3-carboxylic acid.⁵⁷ 2-Phenyl-6-methylquinoline yielded 8 per cent of the 6-carboxylic acid.⁵⁸ 2-*p*-Tolylquinoline gave no acid and and 37.5 per cent was not attacked, but considerable tar was formed. Conquinine⁵⁹ sulfate similarly gave 56.0 per cent quininic acid and about 2.6 per cent of a dark resinous substance. Of the base 36 per cent was unaltered, as was 90.9 per cent of the sensitizer.

On long standing in diffuse daylight and more rapidly in sunlight, 6,7-dimethoxy-1-benzyl-N-methyl-1,2,3,4-tetrahydroquinoline-1-carboxylic acid evolves

⁵² Henri, V., and Angenot, P., *Compt. rend.*, **201**, 895 (1935), state that light of wavelengths greater than 2750 Å has no photochemical action on pyridine vapor. Ultraviolet light does not influence the nitration of pyridine in the vapor phase by nitrogen peroxide, Shorugin, P. P., and Topchiev, A. V., *Ber.*, **69B**, 1874 (1936).

⁵³ Koller, G., *Ber.*, **60B**, 1920 (1927); *Chem. Abs.*, **22**, 80 (1928).

⁵⁴ Cantieni, R., *Helv. Chim. Acta*, **17**, 1492 (1934); **18**, 3, 1420 (1935); *Chem. Abs.*, **29**, 1034 (1935); **30**, 1662 (1936).

⁵⁵ Castiglioni, A., *Annali Chim. Appl.*, **27**, 256 (1937); *Brit. Chem. Abs.*, **A** (11), 478 (1937).

⁵⁶ de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).

⁵⁷ John, H., and Behmel, G., *Ber.*, **66B**, 844 (1933); *Chem. Abs.*, **27**, 3713 (1933).

⁵⁸ For the behavior of *p*-methoxyquinoline, see Maschmann, E., *Ber.*, **59B**, 2825 (1926).

⁵⁹ John, H., and Andraschko, E., *Ber.*, **64B**, 1286 (1931); *Chem. Abs.*, **25**, 4275 (1931).

carbon dioxide and changes to a yellow oil no longer soluble in alkali.⁶⁰ Benzylidene quinaldine, exposed to sunlight as a solid or in benzene solution, forms a dimer.⁶¹

Scholl, Semp and Stix⁶² find the arylpyrrolinoanthranolazyls to be nitrogenous, free organic radicals characterized by the absence of all tendency to dimerization, and resembling in stability toward air, acids and alkalis, the common dyes with normal valency. They are unstable toward light, being rapidly decolorized in solution by sunlight.

Histazarin dimethyl ether monoxime is converted by ultraviolet light into a mixture of the *trans* and *cis* forms.⁶³

Visible light hastens the oxidation of N-methylphenazonium salts, producing mainly the 4-ketocompound, pyocyanine and phenazine, with small amounts of 2-hydroxyphenazine and 2-keto-N-methylphenazine. Photochemical oxidation of the ethosulfate yields 4-keto-N-ethylphenazine.⁶⁴

ALKALOIDS

Lesure⁶⁵ found considerable ultraviolet absorption by solutions of caffeine, eserine salicylate, apomorphine hydrochloride, and quinine bisulfate. Solutions of eserine salicylate and apomorphine hydrochloride were only slightly discolored and no polarimetric change was observed after an exposure of 15 to 30 minutes. Solutions of cocaine hydrochloride or 1-per cent quinine bichloride or pilocarpine hydrochloride were not effected upon exposure for 30 minutes to the light of a Cooper-Hewitt lamp.

Nicotine. This alkaloid, its zinc chloride double salt, isomethiodide and dimethyliodide in water and in cyclohexane all exhibit a strong absorption band at 2650A.⁶⁶

Ultraviolet light produces a change in nicotine solutions.⁶⁷ A 0.1-per cent solution when exposed in a quartz flask at 5 cm. from an ultraviolet source for 15 minutes showed a decided decrease in nicotine content. On the other hand, Custis claimed that a 40-per cent solution of commercial nicotine, when exposed for 30 minutes at 5 cm. from an iron arc showed an increase in the amount of nicotine present. Custis assumed that in this case some nicotine had been synthesized from certain oils present as impurities in the commercial sample. Attempts to synthesize nicotine photochemically have not been successful. Irradiating a 2-per cent aqueous solution of formaldehyde in 6.2*N* ammonia with which was admixed some copper carbonate gave, in experiments by Watson and Vaidya,⁶⁸ methylamine but no nicotine. This did not support the view of Bhargava and Dhar that nicotine is formed by the action of light on formaldehyde and ammonia.

The destruction of nicotine has, however, been repeatedly confirmed. In the presence of such sensitizers as potassium chromate, gold chloride, ferric nitrate, iodine and chlorophyll, sunlight causes decomposition of aqueous solutions of the alkaloid, present either as free base, salicylate, tartrate or malonate.⁶⁹ In tobacco,

⁶⁰ Hahn, G., and Stiehl, K., *Ber.*, **69B**, 2627 (1936); *Chem. Abs.*, **31**, 1815 (1939).

⁶¹ Henze, M., *Ber.*, **70B**, 1273 (1937); *Chem. Abs.*, **31**, 5800 (1937).

⁶² Scholl, R., Semp, H., and Stix, E., *Ber.*, **60B**, 1236 (1927); *Chem. Abs.*, **21**, 2684 (1927).

⁶³ Haq, M., Ray, J. N., and Tuffail-Malkana, M., *J. Chem. Soc.*, 1326 (1934).

⁶⁴ McIlwain, H., *J. Chem. Soc.*, 1704 (1937).

⁶⁵ Lesure, A., *J. pharm. Chim.*, **7**, 1,569; *Chem. Abs.*, **5**, 963 (1911).

⁶⁶ Lowry, T. M., and Lloyd, W. V., *J. Chem. Soc.*, 1376 (1929).

⁶⁷ Custis, H. H., *J. Frank. Inst.*, **184**, 878 (1917).

⁶⁸ Watson, H. F., and Vaidya, B. K., *J. Indian Chem. Soc.*, **11**, 441 (1934); *Brit. Chem. Abs.*, **A**, 1116 (1934).

⁶⁹ Plotnikow, J., and Weber, K., *Chem. Ztg.*, **55**, 237 (1931); *Chem. Abs.*, **25**, 2921 (1931).

the rate of destruction was much less. Orange-red light was believed to be the most effective.

It has been found that, after irradiation from a mercury arc, nicotine solutions have partially lost their effect on the blood pressure of dogs.⁷⁰ Wakeham and Tracy⁷¹ found that although the reduction of toxicity might amount to 70 to 75 per cent in 75 minutes, it subsequently returns almost to the original value. Gant⁷² observed that after 105 minutes of irradiation, a 0.1-per cent solution of nicotine had lost its basicity and that after 150 minutes it had acquired a slight acidity. At the neutral point the solution had a slight vasopressor activity. The product contained nicotinic acid, methylamine and unchanged nicotine. After 12 hours of irradiation the solution became neutral again, because of the destruction of the nicotinic acid, malonic acid and methylamine. Traces of nitrates, nitrites and ammonia were then found. The irradiation of nicotinic acid gave rise to the same end products. During the irradiation of nicotine, the solution darkened in color. This was ascribed to the formation of yellow oxidation products of nicotinic acid. The color is destroyed by further irradiation.

Quinine. The beautiful fluorescence induced in quinine solutions by visible and ultraviolet light has long been admired. Fabre⁷³ employed it in measuring the rate of elimination of quinine in the urine.⁷⁴ Similar fluorescence methods apply also to hydrastinine and other alkaloids.

The exposure of solutions of quinine salts to ultraviolet rays is said to have no effect on the paralyzing influence of these solutions on *Paramecium* and *Vorticella*,⁷⁵ notwithstanding the view of Roskin and Romanova⁷⁶ that irradiation increases the toxicity. Giordani⁷⁷ holds that, when exposed to ultraviolet rays in the presence of various substances, solutions of quinine undergo transformation into the toxic isomer, quinotoxin. Among the accelerators of the change are urethane and glycerol, which are frequently used in the preparation of solutions for intramuscular or intravenous injection. Alcohol, chloroform and hydrochloric acid were found ineffective in this change.⁷⁸ Macht and Teagarden⁷⁹ found that fluorescent solutions of quinine and quinidine sulfates became pharmacologically more active after ultraviolet irradiation.

Weigert⁸⁰ observed the absorption of oxygen during the irradiation of an aqueous solution of quinine sulfate in contact with air. The reaction velocity increased with increasing concentrations of the quinine sulfate, but was diminished by the addition of an acid. From experiments with gas mixtures containing variable proportions of oxygen, it was found that the reaction velocity increased continuously as the partial pressure of the oxygen diminished. With a mixture of nitrogen and oxygen containing only 0.6 per cent of oxygen, the velocity was about

⁷⁰ Higgins, J. A., Ewing, P. L., and McGuigan, H. A., *J. Pharmacol.*, **42**, 213 (1931); *Chem. Abs.*, **25**, 5934 (1931).

⁷¹ Wakeham, C., and Tracy, G. P., *J. Am. Chem. Soc.*, **55**, 1601 (1933); *J. Pharmacol.*, **44**, 295 (1932); *Chem. Abs.*, **26**, 3301 (1932).

⁷² Gant, V. A., *J. Pharmacol.*, **49**, 408 (1933); *Brit. Chem. Abs.*, **1934A**, 196.

⁷³ Fabre, R., *Bull. soc. chim.*, **7**, 1024 (1925).

⁷⁴ See also Caujolle, F., *Bull. soc. chim. biol.*, **12**, 299 (1930).

⁷⁵ Milanesi, E., *Arch. farm. speriment.*, **46**, 29, 33 (1928); Jirovec, O., and Bouse, V., *Z. Immunitätsf.*, **78**, 100 (1933); *Chem. Abs.*, **27**, 5114 (1933).

⁷⁶ Roskin, G., and Romanova, K., *Z. Immunitätsf.*, **62**, 147, 158; **63**, 452 (1929); *Chem. Abs.*, **24**, 5867 (1930).

⁷⁷ Giordani, K., *Annali chim. appl.*, **18**, 239 (1928); *Brit. Chem. Abs.*, **1928A**, 907.

⁷⁸ For the effect of ultraviolet on monoacyl derivatives of quinic acid, see Josephson, K., *Ber.*, **60B**, 2270 (1927).

⁷⁹ Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, **22**, 21 (1923).

⁸⁰ Weigert, F., *Festschrift W. Nernst*, **1912**, 464; *J. Chem. Soc.*, **102** (ii), 1120 (1912).

thirty times as large as with pure oxygen. The nature of the oxidation process appeared to vary with the proportion of oxygen.

The reaction between quinine and chromic acid has been repeatedly investigated. The early observations of Goldberg⁸¹ seemed to indicate that the velocity is dependent on the extent to which the radiations employed were absorbed by the chromic acid. Luther and Forbes⁸² found, however, by using monochromatic radiations, that quinine is the substance which is light-sensitive, the chromic acid acting only as a filter. The total reaction velocity is proportional to the concentration of the hydrogen ion. The reaction appeared to occur in two stages: (1) the formation of "sensitized" quinine with a velocity proportional only to the light absorbed and (2) a reaction between this product and chromic acid with a velocity proportional to the concentration of the latter and of sulfuric acid.

Forbes and co-workers have conducted an elaborate series of investigations on the quantum yield at seven wave-lengths.⁸³ The quantum yields change with sulfuric acid concentrations at 4050, 3660, 3130 and 2800Å and cannot be correlated with the effect of the acid on the extinction of either the quinine or the dichromate. Since the extinction coefficients are additive, it appears improbable that a stable complex is formed, analogous to that of uranyl oxalate. Instead, the reaction occurs in photochemically efficient clusters in the sense in which the term had been employed by Weigert. Irradiation of the dichromic acid did not increase its tendency to react with non-activated quinine, except possibly at wave-lengths shorter than 2800Å. The temperature coefficient of the reaction is 1.12. By graphical methods, the reaction order was found to be zero for quinine and 0.43 for dichromic acid or 0.86 for chromic acid. For sulfuric acid, it is only 0.07, indicating a subordinate role for this reactant. Ten quinine derivatives appear to give similar quantum yields. The values are of the order of 0.065 to 0.027 for quinine and most of the other alkaloids except cinchonine and cinchonidine, for which they are smaller. The low values are not due to the direct photolysis of the alkaloid. Probably a quantum is first absorbed by the quinoline group of the molecule for the logarithm of the quantum yield, at least in the case of quinine, is a linear function of the logarithm of the concentration of excited molecules. The activated molecules then reduce the chromic acid, one activated quinine molecule reacting with one of chromic (not dichromic) acid. In the case of all the alkaloids tested, the secondary hydroxyl group of the activated molecule appeared to be chiefly responsible for the reduction of the chromic acid. The significant suggestion is made that the energy absorbed by the quinoline group may be transferred to the secondary hydroxyl, this transfer occurring only when various photochemically inactive groups are substituted for hydrogen on the opposite side of the quinoline group. The energy transfer may be a resonance phenomenon.^{83a} Quinine does not react at 4360Å, where absorption is negligible, but decomposes at 4050Å where absorption is considerable. With cinchonine, no photolysis occurs at 4050, but does occur at 3660Å. With vuzin, the shift is toward the red; absorption is marked at 4360Å. The quantum yield decreases as the number of quanta absorbed

⁸¹ Goldberg, E., *Z. wiss. Phot.*, **4**, 95 (1906); *J. Chem. Soc.*, **90** (ii), 514 (1906).

⁸² Luther, R., and Forbes, G. S., *J. Am. Chem. Soc.*, **31**, 770 (1909).

⁸³ Forbes, G. S., Woodhouse, J. C., and Dean, R. S., *J. Am. Chem. Soc.*, **45**, 1891 (1923); Morton, D. S., *J. Phys. Chem.*, **33**, 1135 (1929); Forbes, G. S., Heidt, L. J., and Boissonas, C. G., *J. Am. Chem. Soc.*, **54**, 960 (1932); Forbes, G. S., Heidt, L. J., and Brackett, F. P., Jr., *Ibid.*, **55**, 588 (1933); Forbes, G. S., and Heidt, L. J., *Ibid.*, **55**, 2407 (1933). Forbes, G. S., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 1 (1935); *Chem. Abs.*, **30**, 6648 (1936). Accurate absorption data for quinine at various acid concentrations were obtained in the course of this work.

^{83a} Compare the views of Norrish on the simpler molecules of aldehydes.

in the first centimeter of the reaction mixture increases. The yield is a maximum for quinine at 2800A and for cinchonine at 2540A.

Piperidine metavanadate turns black with liberation of piperidine upon irradiation with ultraviolet light.⁸⁴

Light from a quartz mercury lamp causes a change in the absorption spectrum of ergometrine, which may serve to distinguish it from other ergot alkaloids.⁸⁵

Strychnine in sulfuric acid is unaffected by the addition of small amounts of uranyl acetate; but on exposure to sunlight, the solution becomes violet, as a result of oxidation. This method may be used for the detection of 1×10^{-5} part of strychnine.⁸⁶ Under the same conditions of exposure, codeine and morphine give a deep blue color. None of the common alkaloids gives a similar reaction. This blue coloration may also be obtained by using a solution of uranyl acetate which alone has been exposed to the sunlight. This is due to the formation of formaldehyde, the addition of which to a solution of codeine in sulfuric acid with uranium or iron acetates in the absence of sunlight gives an intense blue coloration.

⁸⁴ Baudisch, O., and Gates, F. L., *J. Am. Chem. Soc.*, **56**, 373 (1934).

⁸⁵ Bennekou, I., and Schou, S. A., *Dansk Tids. Farm.*, **10**, 105 (1936); *Chem. Abs.*, **30**, 3944 (1936). See also Harmsma, A., *Pharm. Weekblad*, **65**, 1114 (1928); *Chem. Abs.*, **29**, 235 (1929).

⁸⁶ Aloy, J., Valdigué, A., and Aloy, R., *Bull. soc. chim.*, **39**, 792 (1926); *Chem. Abs.*, **20**, 2952 (1926).

Chapter 28

Effects of Light on Halogenation Reactions

Visible light of short wave-length and ultraviolet rays have long been employed to assist in reactions involving halogenation. Chlorination of toluene in light make benzyl chloride, benzal chloride and benzotrichloride and, by hydrolysis the from, benzyl alcohol, benzaldehyde and benzoic acid, is a procedure of long standing. In fact, this application has received considerable commercial use.

During the World War I there was a shortage of amyl alcohol which stimulated extensive investigations on the chlorination of butane, pentane and hexane to monochlor compounds which in turn could be converted into the corresponding alcohols acetates.¹ Methods based upon these developments have been superseded in practice by entirely different processes, so that these photochemical reactions are at present largely of historical or purely theoretical importance.

It is convenient to discuss halogenation reactions in a separate chapter since they depend for the most part upon the absorption of the light energy by halogens rather than by the organic reactants. In this discussion, the organic compounds are considered in about the order in which their photochemical reactions have been considered in previous chapters. Due consideration must be given to the possibility that in some instances, particularly those in which unsaturated organic compounds play a part, there may be an absorption of light by the organic substance in addition to that absorbed by the halogen.

Schumacher² has reviewed the photochemical reactions of the halogens with aliphatic compounds. Hass, McBee and Weber³ conducted photochemical chlorinations of propane, *n*- and iso-butane and *n*- and iso-pentane at temperatures from -60° to 300° and studied the reaction in the dark at temperatures up to 600°C. They separated the products by distillation and identified them rigorously. When pyrolysis temperatures were avoided, no rearrangements of the carbon skeleton occurred during either the photochemical or the thermal chlorinations. Every possible monochloride derivable without such rearrangement was found to be always formed. This generalization extended to all polychlorides studied. Photochlorination of liquid 1-chloro-3-methyl-propane at 7°C. yields 7 or 14 per cent of overchlorinated product when a given amount of chlorine is added slowly and rapidly.⁴

Although Tolloczko⁵ obtained by the irradiation of streaming mixtures of chlorine and natural gas at 80 to 100°C. by an ultraviolet lamp, such products as methyl chloride, dichloromethane, carbon tetrachloride and di-, tetra- and hexachlorethane, Baskerville and Riederer⁶ found it was the blue rather than

¹ de Lattre, J., *French P.* 468,244, Feb. 9, 1914; *J. Soc. Chem. Ind.*, 33, 953 (1914).

² Schumacher, H. J., *Angew. Chem.*, 49, 613 (1936).

³ Hass, H. B., McBee, E. T., and Weber, P., *Ind. Eng. Chem.*, 27, 1190 (1935); 28, 333 (1936); 29, 1335 (1937).

⁴ Hass, H. B., McBee, E. T., and Hatch, L. F., *Ind. Eng. Chem.*, 29, 1335 (1937).

⁵ Tolloczko, S., *Abhandl. Krakauer Akad. Wissensch.*, 52, 307; *Chem. Zentr.*, 84, 11, 99 (1914).

⁶ Baskerville, C., and Riederer, H. S., *Ind. Eng. Chem.*, 5, 5 (1913).

ultraviolet rays which accelerate the reactions. Brooks, Smith and Essex⁷ found similarly that once the chlorination of pentane had been started, it would proceed very smoothly in diffused daylight. Mott and Bedford⁸ demonstrated that the flaming carbon arc gave more rapid chlorination of isoamyl chloride, isopentane or benzene than did the quartz mercury arc. Furthermore, little efficiency was lost by the use of glass containers when the flaming arc was used.

In subsequent experiments on the chlorination of methane, Bedford⁹ found diffused daylight to produce little or no reaction as long as the percentage of chlorine in the gases was low. Upon suddenly exposing such mixtures to the white flame arc there was an instantaneous explosion of the gases.

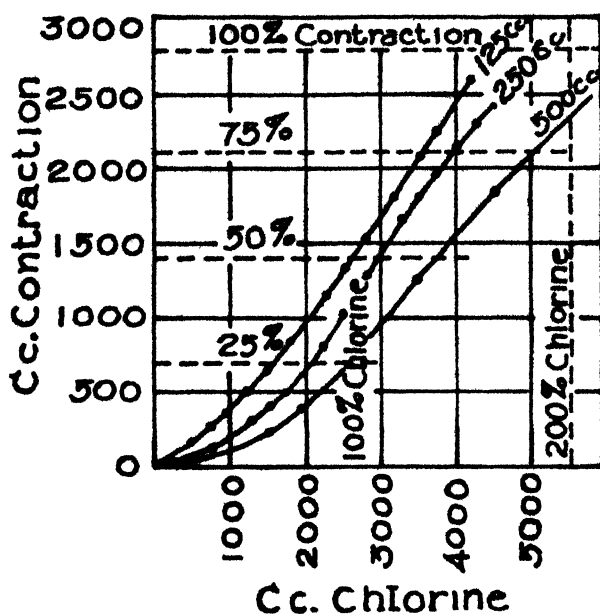


FIGURE 116. Chlorination of Natural Gas.

Figure 116 shows the results reported on the chlorination of natural gas at room temperature in the presence of various quantities of chlorine. After each exposure the gases were cooled by shaking up with water which removed the hydrogen chloride and condensed such reaction products as were liquid at the temperature of the water. The volume of the residual gases was then noted and the contraction from the original gas volume calculated. Starting with three liters of natural gas there was always an unreacting residue of about 200 cc. showing that about 2800 cc. would react with chlorine.*

To avoid the formation of carbon tetrachloride, Bedford tried filling the reaction chamber with cracked ice. He reasoned that in this manner he should obtain only the di- and tri-substitution products, since methyl chloride is a gas at the temperature of ice and the other products might be expected to condense out before forming the tetrachloride. The first experiment, however, indicated the difficulty of securing proper gas circulation. After many variations in the set-up, Bedford employed the apparatus shown

⁷ Brooks, B. T., Smith, D. F., and Essex, H., *Ind. Eng. Chem.*, 10, 511 (1918).

⁸ Mott, W. R., and Bedford, C. W., *Ind. Eng. Chem.*, 8, 1029 (1916).

⁹ Bedford, C. W., *Ind. Eng. Chem.*, 8, 1090 (1916).

* The horizontal dotted lines in Figure 116 represent percentages of the total contraction obtained and aid in the study of the curves.

in Figure 117. An 8-liter, two-necked Woulfe flask, with the bottom removed, was placed over a single ice cake chipped to nearly fill the flask. As the ice melted in the top of the reaction chamber, the flask settled upon it, keeping the ice in the top of the chamber where the cooling is most needed, until the bottom of the flask touched the bottom of the vat. The dotted lines show the point of highest temperature as shown by the melting of the ice. Upon starting the reaction, by means of the white flame arc, with the chlorine content of the gases about one in eight, the circulation was found to be rapid and violent. It was found that 2.6 cubic feet of natural gas gave 166 cc. of reaction products. This is equivalent to about seventeen gallons per thousand cubic feet. This included methylene chloride and chloroform dissolved in the water, which were separated by distillation.

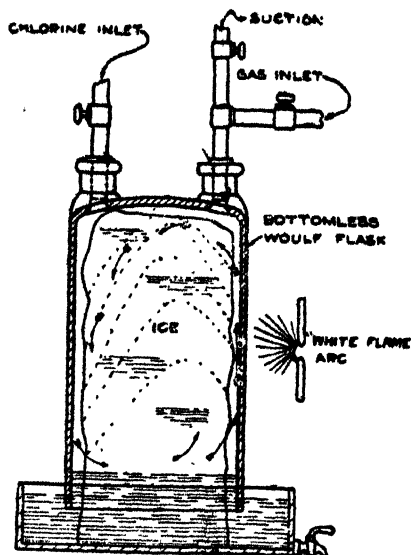


FIGURE 117. Bedford's Apparatus for Chlorination of Methane.

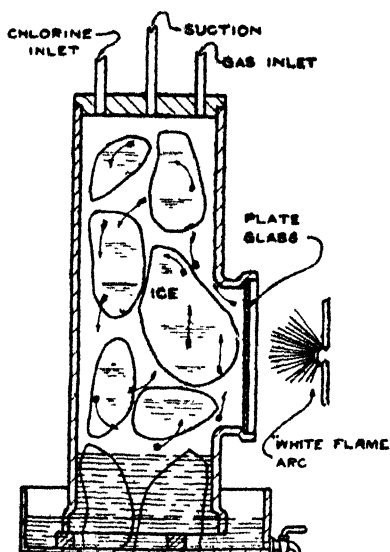


FIGURE 118. Modification of Bedford's Apparatus.

A large wooden reaction chamber, practically duplicating Figure 118, 28" by 28" by 44", inside dimensions, was built for carrying out the reaction on a large scale. In one experiment using 250 cubic ft. of natural gas, the rate of consumption varied from 14 to 30 cubic feet per hour and several gallons of product resulted. The analysis of the liquid reaction product separating out under the water was as follows, the percentages being by volume:

Table 21.—Chlorides from Natural Gas.

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
35	35	5	20

The analysis of the part soluble in the water and separated by distillation was:

60	28	1.5	6
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About 14 per cent of the reaction product dissolves in the water produced from the melting of the ice by the heat of the reaction. This soluble portion may be entirely recovered by distilling off 5 to 10 per cent of the water, the methyl chloride coming over with the distillate, and the residue being about a 5-per cent solution of hydrochloric acid, provided that no water has been added except that produced by the melting of the ice.

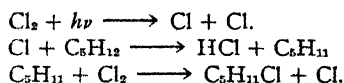
About 135 pounds of ice were necessary for the production of one gallon of product having the composition given above.

According to Padovani and Magaldi,¹⁰ the condition necessary for obtaining a maximum yield of monochloromethane in the photochemical chlorination of methane by use of the mercury arc is to have the ratio of methane to chlorine between 15 to 1 and 19 to 1. Then up to 29 per cent of chlorine goes to methyl chloride and 80 per cent of the total chlorine is utilized. The ratio of methyl chloride to chlorine present in liquid products is 1.75. The efficiency of energy utilization is extremely low. This is the most serious obstacle to the commercial utilization of the process.

Comparatively few theoretical studies have been made of these chlorination reactions. In the case of methane, the chlorination is a chain process, quantum yields of 10^4 being found.¹¹ The reaction is strongly inhibited by traces of oxygen.

From an analogy between this reaction and the hydrogen-chlorine combination, Jones and Bates¹² suggest that it occurs by virtue of chlorine atoms and free methyl radicals, the latter formed by the action of the chlorine atom on methane. From their rate experiments, conducted with a flowing system in a glass spiral illuminated by a Pyrex mercury arc, they were unable to determine whether the methyl group or a hydrogen atom carried the chains. Simple considerations of the collision mechanism of a chlorine atom with the methane molecule made the former seem the more probable.

The total chlorination of pentane in the liquid phase and with rigid exclusion of oxygen which is an inhibitor was studied by Stewart and Weidenbaum.¹³ Using light of 3650A, they found a quantum efficiency of 192. The reaction rate is proportional to the chlorine concentration at constant light intensity. The mechanism involves the reactions:



This mechanism fulfills the necessary conditions that the overall reaction, as well as every step, be exothermic or have but a small energy of activation. The correct experimental rate law is derivable if the chain-terminating step is taken to be a formation of chlorine molecules at the wall or inert molecules.

Benrath and Hertel¹⁴ found that perfectly purified and dried carbon tetrachloride contains free chlorine after several days of exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a solvent in which to study the photochlorination of various aliphatic compounds. Since halogen compounds are frequently used as solvents, it may be noted that chloroform is comparatively unstable under the influence of ultraviolet radiation¹⁵ and further that trichloroethylene is on occasions a somewhat fickle solvent disengaging hydrogen chloride.¹⁶

During the period from 1912 to about 1925 a considerable number of patents dealing with the chlorination of various saturated hydrocarbons were issued. It

¹⁰ Padovani, C., and Magaldi, F., *Giorn. Chim. Ind. Applicata*, **15**, 1 (1933); *Chem. Abs.*, **27**, 3443 (1933).

¹¹ Coehn, A., and Cordes, H., *Z. physik. Chem.*, **9B**, 1 (1930).

¹² Jones, L. T., and Bates, J. R., *J. Am. Chem. Soc.*, **56**, 2282 (1934).

¹³ Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.*, **57**, 1702 (1935).

¹⁴ Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

¹⁵ Kailan, A., *Monatsh.*, **38**, 537 (1917); *J. Chem. Soc.*, **112**, i, 209 (1917).

¹⁶ Elsner, W., *Chem. Z.*, **41**, 901 (1917).

is feasible here to do no more than cite these, since most deal with details of apparatus for applying ultraviolet rays.¹⁷

Graul and Hanschke¹⁸ boiled normal hexane in an enameled vessel on a water-bath, and passed the vapors through a vertical fractionating column into a second vessel in which they were mixed with chlorine. The mixture, containing an excess of hexane vapor, passed into a third vessel in the middle of which a mercury lamp was burning. The vapors leaving this reaction vessel were passed through a condenser in which the chlorhexane and the excess of hexane condensed and passed through a siphon into a

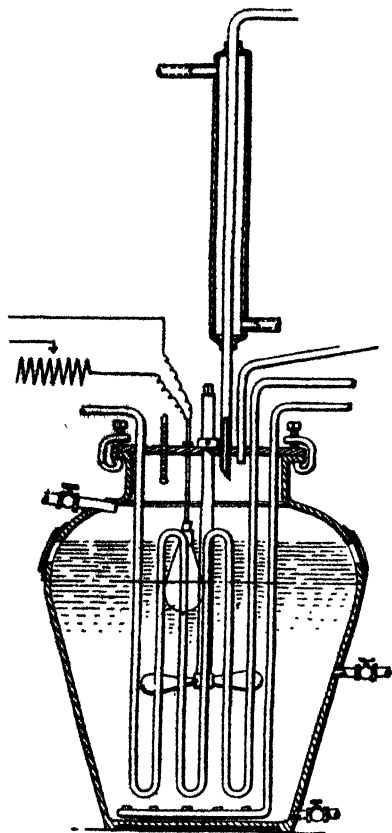


FIGURE 119.

Apparatus of Brooks, Essex and Smith for Chlorinating Liquid Hydrocarbons.

distillation vessel, while the hydrochloric acid formed during the process was allowed to escape from the circuit. The fractionating column attached to the first vessel was maintained at a temperature that allowed only hexane to pass, while chlorhexane remained in the still and increased in quantity. To prepare monochlor-isoheptane, a Galician petro-

¹⁷ Blanc, C., U. S. P. 1,248,065, Nov. 27, 1917; Rodebush, W. H., U. S. P. 1,402,318, Jan. 3, 1922; Okinaka, T., and Sakai, S., Japanese P. 35,994; *Chem. Abs.*, 15, 1535 (1921); Japanese P. 39,940, July 16, 1921; *Chem. Abs.*, 16, 3560 (1922); DuPont Co., French P. 453,406, June 21, 1913; Pfeiffer, I., and Szarvasy, E., U. S. P. 1,012,149, Dec. 19, 1911; *J. Soc. Chem. Ind.*, 32, 91 (1912); Snelling, W. O., U. S. P. 1,523,563, Jan. 20, 1925; 1,285,823 and 1,325,214; *Chem. Abs.*, 14, 369 (1920); U. S. P. 1,271,790, July 9, 1918; 1,523,563, Jan. 20, 1925; Keyes, F. G., U. S. P. 1,237,652, Aug. 21, 1917; Sparre, F., and Masland, W. E., U. S. P. 1,379,367, May 24, 1921; Tompkins, H. K., British P. 780, Jan. 18, 1915; *J. Soc. Chem. Ind.*, 34, 1225 (1915); Leiser, R., and Ziffer, F., U. S. P. 1,459,777, June 26, 1923; Söll, J., and Runkel, K., German P. 491,316, Dec. 12, 1922; Keyes, F. G., U. S. P. 1,198,356, *Chem. Abs.*, 10, 2315 (1916); Lacey, B. S., U. S. P. 1,308,760; *Chem. Abs.*, 13, 2219 (1919).

¹⁸ Graul, O., and Hanschke, G., U. S. P. 1,032,822, July 16, 1912.

leum fraction consisting chiefly of isoheptane was placed in a lead-lined vessel provided with fractionating column and raised to the boiling point, at a pressure of 50 mm. of mercury. The vapors were mixed with chlorine and passed through a vessel containing a mercury lamp. In order to chlorinate 10 parts of hydrocarbon, about 7 parts of chlorine were necessary. The chlorination product consisted chiefly of a mono-chloro-isoheptane which boils at about 140°C. and contains 26.5 per cent of chlorine. By treating, in a similar manner, the repeatedly purified fraction of Galician petroleum which boils at from 75° to 81°C., a product was obtained boiling between 135° and 145°C., and containing 29.1 per cent of chlorine, whereas pure monochlorohexamethylene contains theoretically 29.8 per cent of chlorine.

A few patents dealt with the chlorination of liquid hydrocarbons. Brooks, Essex and Smith¹⁹ emphasized the necessity of introducing the chlorine in minute bubbles at a point in the liquid remote from that at which the rays of light enter, and agitating so as to maintain a large excess of hydrocarbon in the zone where the reactions occur. It was believed that this led to the production chiefly of monochloro- products (butyl, pentyl and hexyl chlorides) from gasoline, useful in the manufacture of artificial "amyl acetate." (See Fig. 119.) The unchanged oil is separated from the chlorides by fractional distillation. If dichlorides are to be produced, the container is charged with monochlorides rather than with hydrocarbons. Even solid materials as paraffins may be used if they are melted or dissolved in carbon tetrachloride.

Brooks and Padgett²⁰ chlorinated solar oil in this manner and subjected the dichloride obtained to a high temperature in the presence of a catalyst. This treatment split off hydrochloric acid and produced unsaturated hydrocarbons with an iodine number of from 120 to 150 suitable for the formation of "drying" films like those of linseed oil.²¹

After a lapse of nearly ten years, patents in this field have again begun to appear. In a continuous flow method for the vapor phase photochlorination of the saturated aliphatic hydrocarbons with three to five carbon atoms, as butane or isobutane, Britton, Coleman and Hadler²² employ surfaces in contact with the reacting mixture cooled to a temperature (below 250°) which prevents the formation of chloroölefines. For preparing monochloro- derivatives, Teichmann, Klein and Rathemacher²³ treat a paraffin hydrocarbon material, such as a pentane fraction, in the liquid phase while exposed to ultraviolet light with a reagent consisting of polychloro- derivatives of the hydrocarbons. The reaction products are then submitted to a reaction with chlorine under such pressure as to maintain the reaction products in the liquid phase, so that monochloro- and polychloro- compounds and hydrogen chloride are formed. The hydrogen chloride is removed and the chloro-compounds separated into two fractions, one containing the mono- and the other the polychloro- derivatives.

According to Sharp,²⁴ a material containing a high percentage of propane and a compound such as the lower chloropropanes convertible into a trichloropropane are treated with chlorine in the presence of a chlorination catalyst such as copper chloride or ferric chloride under the influence of actinic rays, and in a plurality of stages at increasing temperatures.

In their studies of the higher polychlorides obtainable by the chlorination of 2-chloro-2-methylpropane in the liquid phase, Rogers and Nelson²⁵ used ordinary incandescent lamps for activation. They were chiefly concerned with the characterization of the various higher chlorides obtainable by fractional distil-

¹⁹ Brooks, B. T., Essex, H., and Smith, D. F., U. S. P. 1,191,916, July 18, 1916.

²⁰ Brooks, B. T., and Padgett, F. W., U. S. P. 1,220,821, March 27, 1917.

²¹ Details of another chlorination process involving both liquid and vapor phase chlorination successively have been given by Boyd, H. T., U. S. P. 1,293,012, Feb. 4, 1919.

²² Britton, E. C., Coleman, C. H., and Hadler, B. C., U. S. P. 1,954,438, April 10, 1934, to Dow Chemical Co.; *Chem. Abs.*, **28**, 3739 (1934).

²³ Teichmann, C. F., Klein, H., and Rathemacher, C. P., U. S. P. 2,015,044, Sept. 17, 1935; *Chem. Abs.*, **29**, 7338 (1935).

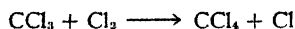
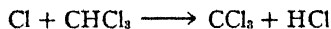
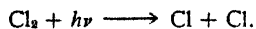
²⁴ Sharp, W. E., U. S. P. 2,001,039, Aug. 6, 1935; *Chem. Abs.*, **29**, 6252 (1935).

²⁵ Rogers, A. O., and Nelson, R. E., *J. Am. Chem. Soc.*, **58**, 1027 (1936).

lation. There were obtained from 3500 cc., 305 cc. of $(\text{CH}_3)_2\text{CClCH}_2\text{Cl}$, 600 cc. of $(\text{CH}_3)_2\text{CClCHCl}_2$, 875 cc. of $(\text{CH}_3)_2\text{CCl}(\text{CH}_2\text{Cl})_2$, 460 cc. of 1,1,2,3-tetrachloro-2-methylpropane and 130 cc. of $\text{ClC}(\text{CH}_2\text{Cl})_3$. Chlorination of 400 cc. of the first fraction of these gave 140 gm. of $(\text{CH}_3)_2\text{CClCCl}_3$. Chlorination of the $\text{CH}_3\text{CH}(\text{CH}_2\text{Cl})_2$ gave the 1,2,3-trichloro- and 1,1,2,3-tetrachloro- derivatives. $(\text{CH}_3)_2\text{CClCH}_2\text{Cl}$ gave the 1,1,2- and the 1,2,3-trichloro- derivatives. In general, the presence of a chlorine atom on a carbon atom promoted further substitution on that atom.²⁶

Chlorination of Chloroform. Gault and Truffault²⁷ found chlorine without action on chloroform in the dark or when exposed to radiations of wave-length longer than about 6390Å. Violet light had a slight effect and ultraviolet rays (3000 to 3400Å) a great one. The reaction begins at -5°C . and becomes rapid at $5-10^\circ\text{C}$. Dry chlorides of calcium, zinc or aluminum act to some degree as catalysts, but ferric chloride appeared to inhibit the reaction entirely by acting as an internal filter. Even in the absence of any stimulus other than ultraviolet, the reaction is complete and carbon tetrachloride results. Benrath and Hertel²⁸ observed an induction period of about thirty minutes when the reaction was carried out in carbon tetrachloride.

In the vapor state, the rate of the reaction at 50 to 70°C . is proportional to the square root of the chlorine concentration and to the square root of the absorbed energy.²⁹ The temperature coefficient is 1.45 between 50 and 60°C . Oxygen practically suppresses the formation of carbon tetrachloride and yields phosgene. The reaction has a chain mechanism, with the following four reactions:



Chapman³⁰ finds the average quantum yield of hydrogen chloride 1.70 in the chlorine-sensitized photooxidation of chloroform in carbon tetrachloride solution; in the vapor phase it is about 100.

In the replacement of bromine by chlorine in bromotrichloromethane, Noddack³¹ reported a quantum yield of unity at high concentrations. This was decreased to about 0.2 when dilute solutions were used. A later study by Grüss³² indicated a value of 0.88, independent of the concentration. These workers assumed that the reaction is a simple replacement, and determined the rate of the change by measuring the absorption changes which attended the liberation of the bromine. The possibility that an error might arise because of the formation of a bromochloride led Vesper and Rollefson³³ to examine the reaction again. They found the reaction more complicated than had been assumed, a chain process being involved. They employed the group of lines at 3660Å isolated from the mercury

²⁶ For the chlorination of methyl chloride and dichloromethane, see Dachlauer, K., and Schmitzler, E., French P. 816,990, Aug. 21, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 32, 2142 (1938); German P. 657,978, May 25, 1938; *Chem. Abs.*, 32, 5856 (1938).

²⁷ Gault, H., and Truffault, R., *Compt. rend.*, 179, 467 (1924); *Chem. Abs.*, 19, 35 (1925).

²⁸ Benrath, A., and Hertel, E., *Z. wiss. Phot.*, 23, 30 (1924).

²⁹ Schumacher, H. J., and Wolff, K., *Z. physik. Chem.*, 25, 161 (1934). See, however, Schwab, G. M., and Heyde, V., *Z. physik. Chem.*, B8, 147 (1930).

³⁰ Chapman, A. T., *J. Am. Chem. Soc.*, 56, 818 (1934).

³¹ Noddack, W., *Z. Elektrochem.*, 27, 359 (1921).

³² Grüss, H., *Z. Elektrochem.*, 29, 144 (1923).

³³ Vesper, H. G., and Rollefson, G. K., *J. Am. Chem. Soc.*, 56, 1455 (1934).

arc radiations by means of a filter, in order to avoid the decomposition of bromotrichloromethane which Paterno⁸⁴ had found to occur in the region below 3350Å. By spectrographic methods and a knowledge of the original chlorine concentration, it was possible to calculate the concentrations of chlorine, bromine and bromine chloride present at any time. The reaction was found to be



no hexachloroethane being formed. (A second reaction in which free bromine and two molecules of carbon tetrachloride are formed occurred to only a negligible extent.) The rate of the reaction varied directly with the chlorine concentration raised to a power between 1. and 1.5, and with the bromotrichloromethane concentration to a power somewhat greater than 0.5. The rate was markedly retarded by bromine chloride. It was not affected by the total pressure, but was doubled by increasing the temperature from 28 to 50°C. No dark reaction occurred. The incident light intensity enters the rate law by a power slightly greater than 0.5. Inert gases had practically no effect on the reaction rate. The quantum yield was found to be much higher than previous workers had indicated. It reached at least thirty at the beginning of the reaction but decreased to less than ten when the concentration of the bromine chloride had become large. The quantum yield could be decreased by lowering the concentrations of either of the two reactants.

A little attention has been devoted to iodination reactions of the saturated simple paraffins. Iodine derivatives of the paraffin series, excepting liquid methane, may be obtained by mixing the hydrocarbon in the dark with hydriodic acid and subjecting the mixture to the action of light rays of short wave-length or to the silent electric discharge. The reaction temperature may be reduced, according to the Badische Co.³⁵ by operating under diminished pressure.

The photochemical formation of phosgene in the action of chlorine on chloroform in the presence of oxygen is inhibited by such substances as methanol, ethanol and ammonia. The duration of the inhibition is proportional to the quantity of the inhibitor.³⁶ It is due to the removal of the chlorine atoms by the inhibitor, since, if the latter is first chlorinated, it ceases to affect the reaction.

UNSATURATED HYDROCARBONS

A few early patents were devoted to the chlorination of unsaturated hydrocarbons. Eldred and Mersereau³⁷ state that olefins produced by cracking oil may be treated with chlorine in the presence of rays of a mercury-vapor lamp in order to obtain chlorinated products. They noted that the operation requires caution since the reaction is violent. Ragaz, Paillard and Briner³⁸ passed 30 cc. of kerosene over iron turnings in an iron tube at temperatures of 550 to 800°C. and obtained about 13 liters of gas containing about 30 per cent of unsaturated compounds. By passing a slight excess of chlorine into the gas as it was formed in diffused daylight about 57 per cent of the gas was converted into a mixture of chlorinated hydrocarbons. This gave fractions distilling at 65-100°C., 70.69 per cent chlorine; 100-125°C., 73.41 per cent; 125-150°C., 75.14 per cent. These were mobile fluids whose flash points were 5°C., 19°C. and 36°C., respectively.

⁸⁴ Paterno, E., *Jahresh. Chem.*, **24**, 259 (1871).

³⁵ Badische Anilin u-Soda Fabrik, German P. 266,119, Oct. 31, 1911.

³⁶ Schumacher, H. J., and Sundhoff, D., *Z. Elektrochem.*, **21**, 499 (1935).

³⁷ Eldred, B. E., and Mersereau, C., U. S. P. 1,234,886, July 21, 1917.

³⁸ Ragaz, Y., Paillard, H., and Briner, E., *Helv. Chim. Acta*, **8**, 225 (1925); *J. Soc. Chem. Ind.*, 1925B, 580.

They readily dissolved sulfur, iodine or white wax. The use of ultraviolet light or the addition of catalysts did not improve the yield of non-flammable solvents.

In a patent of the I. G. Farbenindustrie³⁹ 1,1,2-trichloroethane is obtained by direct addition of vinyl chloride and chlorine gases without the use of a solvent by the aid of light or heat.

The rate of addition of chlorine to ethylene is accelerated by the rays of the mercury arc.⁴⁰ Trichlorohydrin is obtained by further chlorination, in the presence of a sulfur compound such as sulfur dioxide, sulfur chloride, sulfonyl chloride, of propylene chloride or a similar compound obtained by saturating unsaturated hydrocarbons with chlorine.⁴¹ The sulfur compound should not exceed 1 per cent of the amount of chlorine. Sulfur dioxide and chlorine may either be introduced separately or mixed. The reaction is effected in direct sunlight or ultraviolet rays or the light of the flaming arc. The product is separated from any unchanged propylene chloride by distillation.

In the chlorination of propylene dichloride with metallic iron present, ultraviolet light and low temperatures favor the production of $\text{CHCl}(\text{CH}_2\text{Cl})_2$. Higher temperatures without irradiation favor the formation of $\text{CHCH}_3\text{Cl}.\text{CHCl}_2$.⁴²

Stewart and Weidenbaum⁴³ investigated the reaction between chlorine and ethylene, using light from a 500-watt tungsten lamp and filters. At 4360A the quantum yield appeared to be large. During the early part of the reaction there appeared to be a logarithmic relation between the chlorine pressure and the time, as well as a linear relation between the reaction rate and the light intensity. The experimental results could be expressed by mechanisms involving either atomic chlorine or Cl_3 ; the collision efficiency of ethylene with either should be high, since the reaction rate is independent of the ethylene concentration over wide limits. The rate was thought to be determined by the rate of liberation of atomic chlorine from an intermediate, $\text{C}_2\text{H}_4\text{Cl}_3$. Any hydrogen added to the reaction vessel appeared not to react until the ethylene-chlorine reaction had gone to completion. When the reaction was carried out in solution in ethylene dichloride, it was very rapid and less than 10 per cent of the chlorine was involved in substitution reactions. But with pentane as the solvent, from 37 to 73 per cent of the chlorine entered into substitution and this could be increased by increasing the ethylene-to-chlorine ratio.

Dickinson and Leermakers⁴⁴ found it possible to chlorinate tetrachloroethylene in carbon tetrachloride solution by the action of blue light in the absence of oxygen. The chlorination proceeds as a chain reaction with a large quantum yield (300-2500) and at a rate proportional to the square root of the intensity of illumination. In the presence of oxygen, in place of a simple inhibition, there occurs a chlorine-sensitized oxidation to trichloroacetyl chloride and phosgene.⁴⁵ This reaction proceeds in solution with a comparatively small quantum yield (1 to 2.5) and at a rate proportional to the light intensity, and to the chlorine concentration.⁴⁶ The work on the chlorination of tetrachloroethylene has been extended

³⁹ British P. 298,084, Sept. 30, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 122 (1929)

⁴⁰ Kinumaki, S., *J. Chem. Soc. Japan*, **54**, 142 (1933); *Chem. Abs.*, **27**, 2369 (1933).

⁴¹ British P. 168,676, Feb. 18, 1921, to Glysyn Corporation; *Chem. Abs.*, **17**, 771 (1923).

⁴² Levine, A. A., and Cass, O. W., *British P.* 471,188, Feb. 28, 1936, to E. I. DuPont de Nemours and Co.; *Brit. Chem. Abs.*, **B**, 1309 (1937).

⁴³ Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.*, **57**, 2036 (1935).

⁴⁴ Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.*, **54**, 3852 (1932).

⁴⁵ Cf. Besson, A., *Compt. rend.*, **121**, 125 (1895).

⁴⁶ See also Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.*, **54**, 4648 (1932).

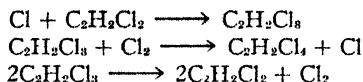
to the gas phase by Dickinson and Carrico,⁴⁷ who conducted it at temperatures below 40°C. and followed the rate by measuring in an ingenious apparatus the change in pressure. In the absence of oxygen, the chlorination proceeded with the formation on the walls of the vessel of colorless crystals having the odor of hexachloroethane. In the presence of oxygen little if any chlorination occurred, but phosgene and trichloroacetyl chloride were obtained. The rate of the chlorination was proportional to the chlorine concentration and to the square root of the intensity of the light absorbed.

In the chlorine-sensitized photo-oxidation in the gas phase about 300 molecules of tetrachloroethylene were oxidized for each quantum (3358Å) absorbed. There was no strong dependence of the yield on the concentrations or light intensity.

The chlorination of *trans*-dichloroethylene at 80-95°C. by the 4358Å line of the mercury arc is a chain reaction.⁴⁸ For a chlorine pressure of 100 mm. and an absorption of 10^{10} quanta per minute, the quantum yield is 7×10^3 and the temperature coefficient 1.13. For pressures of the dichloride greater than 20 mm., the rate is given by

$$\frac{d(\text{C}_2\text{H}_2\text{Cl}_4)}{dt} = k(I_{\text{abs}})^{\frac{1}{2}}(\text{Cl}_2)$$

The mechanism involves the reactions:



The reaction is strongly inhibited by the presence of oxygen.

The reaction with the *cis*- compound is very similar.⁴⁹ In this case, a sensitized oxidation with greater quantum yield does not occur. In the chlorination of trichloroethylene, the rate of formation of pentachlorethane is proportional to the chlorine concentration and the square root of the energy absorbed. Only at pressures below 5 mm. is it dependent on the concentration of trichloroethylene. The temperature coefficient is 1.20. The quantum yield (chlorine at 100 mm. and 1.7×10^{14} quanta per second) is 700. The reaction is inhibited by oxygen and a sensitized oxidation occurs.

Notwithstanding the many instances of inhibition of chlorination processes by oxygen, Willard and Daniels⁵⁰ find the rate of photobromination of liquid tetrachloroethylene with light of 4360Å to be increased by small amounts of oxygen. But when one atmosphere of oxygen is used, the photobromination is almost completely inhibited, probably because of a bromine-sensitized oxidation. The bromination products inhibit the reaction but the concentration of tetrachloroethylene is not important. The quantum yield varies enormously from 24 to only 0.009 (moles of bromine disappearing per quantum) with values of 1 to 5 the most frequent. The free radical $\text{C}_2\text{Cl}_4\text{Br}$ is believed to play a part in the reaction mechanism and it is suggested that the life period of this radical is much shorter at higher temperatures and that it is stabilized by oxygen.

These authors also found that the photobromination of chloroform does not occur at 2650Å in the absence of oxygen, although a reaction takes place in the

⁴⁷ Dickinson, R. G., and Carrico, J. L., *J. Am. Chem. Soc.*, **56**, 1473 (1934); see also Stewart, T. D., and Smith, D. M., *Ibid.*, **51**, 3082 (1929).

⁴⁸ Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **B35**, 285 (1937).

⁴⁹ Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **B35**, 455 (1937); *Z. Elektrochem.*, **43**, 807 (1937).

⁵⁰ Willard, J., and Daniels, F., *J. Am. Chem. Soc.*, **57**, 2240 (1935).

presence of small amounts of the latter. Kaufmann and Hansen-Schmidt⁵¹ found α,β -diiodoethylene to react rapidly with bromine in carbon tetrachloride in light, but not in darkness.

Schultze⁵² briefly called attention to the possibility of a bromine-sensitization of the oxidation of unsaturated hydrocarbons.

The Action of Iodine on Unsaturated Hydrocarbons. Badger and Urmston⁵³ suggested the possibility of separating two types of iodine molecule, only one of which absorbs the 5461A line, by causing the activated type to react photochemically with hexene vapor.

The photosensitizing action of iodine upon the decomposition of ethylene iodide in carbon tetrachloride solution has been studied by Schumacher and Wiig.⁵⁴ The rate is proportional to the concentration of the ethylene iodide and to the square root of the absorbed light energy. At 100°C. the temperature coefficient is 1.57 per 10°. The mechanism involves a chain of simple type carried by iodine atoms. Murthi⁵⁵ finds their data consistent with every collision between iodine atoms in solution resulting in the formation of iodine molecules. According to Schumacher and Stieger⁵⁶ the quantum yield decreases markedly in the band region at 5461 or 5770A as compared with that at 4360A. Their results indicate that at 5460A and 5780A, excited iodine molecules for the most part give up their energy without dissociating. Murthi⁵⁷ calculates from their data and the assumption that every collision between iodine atoms produces a molecule, that the energy of activation is 12 kcals. as compared with an observed value of 11.8. No steric factor is needed to bring the calculated and observed rates into agreement. Dickinson and Nies,⁵⁸ objected that Schumacher's conclusion that excited molecules in the band region largely lose their energy without dissociating was the result of a failure to take into account possible variations in the absorption of the green and blue lines. They repeated rate measurements at various wave-lengths giving special consideration to the distribution of energy. As a result, they concluded that the rates are only slightly lower in the region of discontinuous absorption than in that of continuous absorption. The rate of the reaction depends only upon the rate of production of iodine atoms, irrespective of whether they are formed by primary dissociation or as a result of collisions of excited molecules, presumably with solvent molecules.

When an equimolar quantity of iodine was added to 0.01 molar solutions of 1-butene in methylene chloride or chloroform and the solutions illuminated, 90 per cent of the iodine disappeared in three hours in the former solvent at -60 to -90°C. and 98 per cent in the latter at -60 to -70°C.⁵⁹ On irradiating the solutions in quartz by a spark between high-tungsten steel electrodes, the iodine was evolved quantitatively within an hour in three stages. At 20°C. for 100 hours, 84 per cent of the iodine was evolved, also in stages.

In the quantitative photoiodination (4360, 5460, 6440A) of the first six simple

⁵¹ Kaufmann, H. P., and Hansen-Schmidt, E., *Arch. Pharm.*, **263**, 32 (1925); *J. Chem. Soc.*, **128**, A(11), 554.

⁵² Schultze, G. R., *J. Am. Chem. Soc.*, **53**, 3561 (1931).

⁵³ Badger, R. M., and Urmston, J. W., *Proc. Nat. Acad. Sci.*, **16**, 808 (1930); *Chem. Abs.*, **25**, 1737 (1931).

⁵⁴ Schumacher, H. J., and Wiig, E. O., *Z. physik. Chem.*, **11B**, 45 (1930).

⁵⁵ Murthi, D. S. N., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Brit. Chem. Abs.*, **A**, 832 (1935); *Chem. Abs.*, **29**, 5351 (1935).

⁵⁶ Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **12B**, 348 (1931).

⁵⁷ Murthi, D. S., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Chem. Abs.*, **29**, 5351 (1935).

⁵⁸ Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).

⁵⁹ Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **58**, 182 (1936).

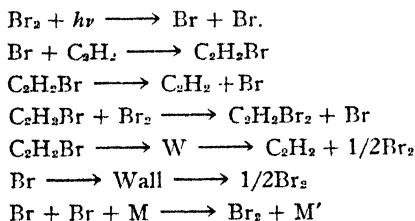
olefins at $-55^{\circ}\text{C}.$, the quantum yields vary as much as forty-fold. They fall off with decreasing frequency of light to the order of 0.01 at 6440Å.⁶⁰ The rate is nearly proportional to the concentrations of olefins and of iodine, and to the light intensity. 1,2-Diiodobutane, prepared at low temperatures, was photolyzed at -60 , -20 and $25^{\circ}\text{C}.$, the quantum yields increasing from 0.7 to 1.15.

DeRight and Wiig⁶¹ find that in red light, a solution of iodine and ethylene in carbon tetrachloride readily yields ethylene iodide, although no dark reaction occurs in 36 hours. The rate depends on the ethylene pressure and falls off with decreasing concentrations of iodine. The reaction probably involves excited iodine molecules. The photodecomposition yields iodine atoms, and the sensitized decomposition proceeds similarly.

The photochemical chlorination of acetylene has been investigated by Peters and Neumann⁶² under a variety of conditions by static and dynamic methods. When mixtures of chlorine and acetylene at pressures up to 50 mm. were illuminated by a mercury arc, the pressure rose after a definite time, and then dropped suddenly, indicating the formation of $\text{C}_2\text{H}_2\text{Cl}_2$ and $\text{C}_2\text{H}_2\text{Cl}_4$. With higher proportions of acetylene, larger proportions of the former compound were obtained. An increase of 30 per cent in the time of illumination increased the chlorine consumption by 5 per cent. The percentage of contraction on illumination increased with the pressure. Pure nitrogen had little effect on the reaction, but nitrogen containing about 5 per cent of oxygen stopped it. In the presence of a large excess of hydrogen, a smaller yield was obtained but there was practically no formation of hydrogen chloride. The explosive process $\text{C}_2\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{C} + 2\text{HCl}$ cannot occur at pressures below 70 mm.

The photobromination of acetylene, in which $\text{C}_2\text{H}_2\text{Br}_2$ is formed, has been studied at $150^{\circ}\text{C}.$ by Booher and Rollefson,⁶³ using the wave-lengths 4358, 5461 and 5791Å. It is a chain reaction with chain length of from about 500 at $150^{\circ}\text{C}.$ to 3000 at $20^{\circ}\text{C}.$ independent of the wave-length. The rate depends on the first power of the light intensity and on powers of the bromine and acetylene concentrations between zero and one. No difference is found in the effect of light of wave-lengths above and below the convergence limit of the bromine bands. The influence of temperature is very small.

These experiments were repeated by Franke and Schumacher,⁶⁴ who minimized the effects of impurities by using greaseless valves and measured the rate by a spiral quartz pressure gauge. Their results differed, but exact rate equations could not be given. The following reactions were suggested as playing a part in the mechanism:



⁶⁰ Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **59**, 693 (1937).

⁶¹ DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **58**, 693 (1936).

⁶² Peters, K., and Neumann, L., *Angew. Chem.*, **45**, 261 (1932).

⁶³ Booher, J. E., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2288 (1934).

⁶⁴ Franke, W. K., and Schumacher, H. J., *Z. physik. Chem.*, **B34**, 181 (1936); see, however, Rollefson, G. K., *Z. physik. Chem.*, **B37**, 472 (1937).

Higher quantum yields (40,000) have since been found at 90°C. and with 100 mm. pressure of each of the reactants.⁶⁵

The bromination of acetylene bromide, by wave-lengths 5460, 4360 and 4060A, is thirty times as fast in the gas phase as in solution in carbon tetrachloride under equivalent conditions.⁶⁶ In both cases, the unimolecular rate constant for the removal of bromine is proportional to the square root of the absorbed energy. The temperature coefficient is 1.4.

Ghosh and Bhattacharya extend the work to include the iodination of phenylacetylene, dicyclopentadiene and β -amylene.⁶⁷

OTHER ALIPHATIC COMPOUNDS

Volmar⁶⁸ claimed that methyl sulfate readily undergoes chlorination at ordinary temperatures under the influence of ultraviolet rays and more slowly under the influence of the light from an arc lamp or a metal filament lamp, the product in all cases being methyl chloromethyl sulfate. The fixation of a second chlorine atom was not observed. It was thought to require radiations of such a wave-length that the dichloromethyl sulfate would be decomposed as it formed.

The bromination of ethyl alcohol occurs under the influence of light.⁶⁹ The reaction is retarded by potassium bromide. A satisfactory mechanism has not yet been proposed. Berthoud believes C_2H_5O may function as an intermediary. In the case of propyl, isopropyl and butyl alcohols the quantum yields are large (5660, 6800 and 8500A).⁷⁰ They increase with temperature and decrease with increasing wave-lengths. The rate of the reaction increases with the amount of light energy-absorbed. At these longer wave-lengths the primary reaction is believed to be the activation of bromine molecules. The temperature coefficients were found to be above two in most cases. With Bhagwat, Malaviya and Dhar⁷¹ found the rate of the reaction with propyl alcohol to be proportional to the square root of the light intensity at 6800A and nearly so at 8500A, but directly proportional to it at 5660A. On the other hand, with isopropyl and butyl alcohols, the rates were proportional to the square root at 6800A and directly proportional to it at 5600 and 8500A. In all cases the reaction is retarded by potassium bromide, and the rates are then proportional to the square roots of the intensities.

The rate of addition of iodine to allyl alcohol in aqueous solution is not influenced by light, but with carbon tetrachloride as solvent there is a photochemical reaction similar to the photobromination.⁷²

Monochloropinacolone has been prepared by treating pinacolone in carbon tetrachloride with chlorine in a quartz flask exposed to strong ultraviolet light.

⁶⁵ Müller, K. L., and Schumacher, H. J., *Z. physik. Chem.*, **B39**, 352 (1938), **B40**, 318 (1938).

⁶⁶ Ghosh, J. C., Bhattacharya, S. K., and Bhattacharya, S. C., *Z. physik. Chem.*, **B32**, 145 (1936). For the bromination of dichloroacetylene, Ghosh, J. C., Bhattacharya, S. K., and Murthi, M. L. N., *J. Indian Chem. Soc.*, **14**, 425 (1937); *Brit. Chem. Abs.*, **A1**, 627 (1937).

⁶⁷ Ghosh, J. C., and Bhattacharya, S. K., *Science and Culture*, **3**, 120 (1937); *Chem. Abs.*, **32**, 414 (1938).

⁶⁸ Volmar, *Bull. soc. chim.*, **27**, 181 (1920); *J. Chem. Soc.*, **118**, (I), 661 (1920); *Chem. Abs.*, **14**, 3406 (1920).

⁶⁹ Bugarski, S., *Z. physik. Chem.*, **71**, 705 (1910); Berthoud, A., and Béranek, J., *J. chim. phys.*, **25**, 28 (1928).

⁷⁰ Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 418 (1931); *Chem. Abs.* **25**, 5846 (1931).

⁷¹ Bhagwat, W. V., Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 406 (1931); *Chem. Abs.*, **25**, 5846 (1931).

⁷² Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

⁷³ Hill, G. A., and Kropa, E. L., *J. Am. Chem. Soc.*, **55**, 2509 (1933).

It is a highly lachrymatory ketone.⁷³ Hill and Kropa also find that colorless monobromopinacolone, when exposed for six hours to ultraviolet light, becomes yellow and then orange. Most of the material is unchanged but some dibromopinacolone can be obtained.

Acids and Their Salts. In the manufacture of lethal gases in Germany during the war, Carr⁷⁴ states, the preparation of diphosgene proved very troublesome. Methyl formate was chlorinated in vessels furnished with chlorine pipes and carefully lined first with lead and then with two layers of tiles. The cement was said to consist of powdered fireclay, asbestos and sodium silicate. These precautions were necessary because any metal introduced onto the mixture from the reaction vessel acts as an anticatalyst. The temperature had to be carefully controlled during the reaction to obtain the best results. As a source of light, which was necessary, an Osram lamp of 4000 c.p. was used. The reaction took from six to eight days for completion.

In the process of chlorination of methyl chloroformate described by Kling, Florentin, Lassieur and Schmutz,⁷⁵ methyl chloroformate is first prepared by the action of carbonyl chloride on methyl alcohol at as low a temperature as possible, a small amount of dimethyl carbonate being formed as a by-product. No matter whether the chlorination takes place in sunlight, arc light, or the light of an incandescent lamp, the monochloroester is obtained almost free from the dichloro-compound which, having almost the same boiling point, is very difficult to remove. Further chlorination gives the dichloroester which is easily fractionated from the trichloroester which is also formed. Chlorination to the limit gives the latter. Methyl formate may also be used as the starting material, giving practically the same products.

Grignard, Rivat and Urbain⁷⁶ state that chlorination of methyl chloroformate in diffused light gives only the chloromethyl ester, and that bright sunlight is necessary for the formation of the di- or trichloromethyl ester. In ultraviolet rays, the trichloromethyl ester is easily obtained. The effect of temperature is such that up to 110-112°C. the chlorination proceeds smoothly; from 113-114°C., it slackens very noticeably. At 117°C. decomposition begins to take place, with the formation of carbonyl chloride. Catalysts, such as ferric chloride, antimony chloride, etc., are initially beneficial in the formation of dichloromethyl ester, but when a certain concentration has been reached, decomposition commences, and may continue indefinitely, since some of the perchloride becomes dissolved in the liquid and continues its action.

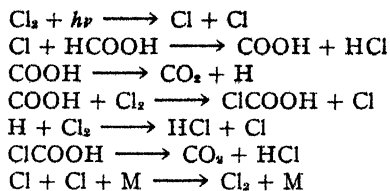
Formic acid itself is chlorinated with quantum yields of about 2000 when the 3650A mercury lines are employed. These lines do not affect the acid but only the chlorine in the primary process. West and Rollefson⁷⁷ find evidence for the production of an unstable intermediary product, chloroformic acid. If this is destroyed by heat or if there is an excess of chlorine, hydrochloric acid and carbon dioxide are the only products. There is no appreciable difference in reactivity between the single and double molecules of formic acid. For the former the reactions involved may be:

⁷⁴ Carr, F. H., *J. Soc. Chem. Ind.*, **38**, 468R (1919).

⁷⁵ Kling, A., Florentin, D., Lassieur, A., and Schmutz, R., *Compt. rend.*, **169**, 1046 (1919), *Chem. Abs.*, **14**, 738 (1920).

⁷⁶ Grignard, V., Rivat, G., and Urbain, E., *Compt. rend.*, **169**, 1074, 1143 (1919); *J. Chem. Soc.*, **118**, 1138 (1920).

⁷⁷ West, H. L., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58**, 2140 (1936).



A similar mechanism can be given for the reaction with the double molecules.

In the chlorination of acetic acid in a quartz flask under the influence of rays from an iron arc, Custis⁷⁸ found that the yield of monochloroacetic acid is improved by the use of red phosphorus as a catalyst. No reaction was observed when the light from an ordinary projection lantern replaced the iron arc. No results were obtained by passing the chlorine gas through a quartz tube irradiated with ultraviolet light before passing it into a non-irradiated flask containing glacial acetic acid.

Benrath and Hertel found that acetyl chloride and isobutyric acid behave similarly to acetic acid. With propionic acid and with ethyl malonate, the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen had been replaced. The second atom then reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were replaced in *n*-butyric acid, both at logarithmic rates, the steps of the reaction being markedly distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom and then, after slowing up, the second atom was replaced at a logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rates were neither linear nor logarithmic. Some of the results indicated a tendency toward periodicity.⁷⁹

In the photobromination of lactic acid, Ghosh and Basu⁸⁰ found it impossible to get regular values for a monomolecular rate constant. It appeared that the quantum yield was low, about 0.25, but the measurements were not considered very accurate since about two-thirds of the transformation appeared to be due to the thermal reaction. Much more regular results were obtained in the case of calcium lactate, but even in this case the dark reaction accounted for about 75 per cent of the observed velocity. Increasing the concentration of the salt increased the velocity constant, but increasing the bromine concentration made the constants irregular, the reaction tending to degenerate into one of zero order. When the concentration of the salt is small (0.03*N*), the quantum yield is about 0.5, but this becomes unity when the concentration is increased to 0.06*N*.⁸¹

Purkayastha⁸² finds that in the bromination of organic acids, there is an induction period which vanishes in the presence of potassium bromide. The quantum yields, higher than those of other observers, possibly because of elimination of oxygen, are for light of 4700Å, 15 (lactic acid), 13 (phenyl-lactic acid), 13 (mandelic acid) and 3 (citric acid). The induction period is ascribed to the formation of complexes between bromine and the reacting acid. The velocity con-

⁷⁸ Custis, H. H., *J. Frank Inst.*, **184**, 874 (1917), see also Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

⁷⁹ See, however, Plotnikow, J., *Z. wiss. Phot.*, 2379 (1924).

⁸⁰ Ghosh, J. C., and Basu, K., *Quart. J. Indian Chem. Soc.*, **2**, 39 (1925); *Chem. Abs.*, **20**, 43 (1926).

⁸¹ For temperature coefficients in various solvents, see Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Chem. Abs.*, **24**, 1035 (1930).

⁸² Purkayastha, R. M., *J. Indian Chem. Soc.*, **6**, 361, 375, 385 (1929); **7**, 991 (1930); *Chem. Abs.*, **23**, 5420 (1929); **24**, 784 (1930); **25**, 2922 (1931).

stants vary inversely with the square root of the incident intensity of the blue light. At 5420, 4880, 4480, 4080 or 3650A, the order is zero molecular.

In the case of the bromination of tartaric acid in aqueous solution, the Indian workers⁸³ found an induction period of two days. The unimolecular rate constant decreased as the initial concentration of bromine was increased, and increased with that of tartaric acid, the more so when part of the acid was replaced by the acid salt. It diminished when hydrobromic acid was added before exposure, decreased with time and increased rapidly with increase in frequency of light employed. It varied approximately as the square root of the light intensity. The quantum yield was high, bromine atoms being involved in the mechanism. These reacted with oxygen (present in solution or liberated by the photochemical reaction of bromine molecules with water) at a rate directly proportional to the oxygen concentration and to the square of the bromine atom concentration. Photoinhibitors were also destroyed by reacting with bromine atoms. The temperature coefficient of the velocity is high, 4.6 per 10°C.

Prik⁸⁴ chlorinated impure methyl stearate in diffused light without a catalyst until it contained 2.5 atoms of chlorine per molecule. When heated to 100°C. with zinc dust, this product split off 12 per cent of its chlorine.

The reactions of bromine and of iodine with oxalic acid have been discussed in Chapter 22. In the case of the chlorination by wave-lengths 4650, 5650, and 7304A, Bhattacharya and Dhar⁸⁵ find the temperature coefficients to be 2.3, 2.4 and 2.5. The quantum yields are 8.6, 7.2 and 4.9, there being little difference in the reaction as conducted by absorption in the band or continuous spectral regions. In a later reinvestigation of this reaction, they, with Mukerji,⁸⁶ concluded that in the absence of potassium iodide the thermal and the photochemical reactions are uni- and semi-molecular, respectively. The reaction rate is not a constant function of the light intensity. Stirring increases the rate and reduces the temperature coefficient, which is the smaller the greater the acceleration due to light.

The addition of bromine to maleic and fumaric acids is not influenced by light, according to Berthoud and Mosset.⁸⁷

When bromine was added to β -phenylpropionic acid in cold chloroform and the reaction allowed to go to completion at room temperature in light, the *cis-trans* ratio in the products was about two to one. In darkness at zero, it was three to two. With the methyl ester, the ratios were one to three and one to two, respectively.⁸⁸

In preparing α -bromo- β -methoxybutyric acids, West and Carter brominate in sunlight an addition product of crotonic acid and mercuric acetate.⁸⁹

Cyclic Compounds. Mono- and di-brom-phenylcyclopropane-1,2-dicarboxylic acids were prepared by Haerdi and Thorpe⁹⁰ by using the rays of a powerful arc lamp. Nicolet and Sattler⁹¹ found that bromine reacts easily with ethyl-

⁸³ Ghosh, J. C., and Mukherjee, J., *Quart. J. Indian Chem. Soc.*, **2**, 165 (1925); *Chem. Abs.*, **20**, 870 (1926); Ghosh, J. C., and Basu, K., *J. Indian Chem. Soc.*, **5**, 343, 361 (1928); *Chem. Abs.*, **22**, 4379 (1928).

⁸⁴ Prik, E. M., *Plasticheskie Massy*, **6**, 26 (1934), *Chem. Abs.*, **29**, 4734 (1935); see also Scheibler, H., and Schmidt, H. J., *Ber.*, **69B**, 12 (1936).

⁸⁵ Bhattacharya, A. K., and Dhar, N. R., *J. chim. phys.*, **26**, 556 (1929).

⁸⁶ Bhattacharya, A. K., Dhar, N. R., and Mukerji, B. K., *J. Indian Chem. Soc.*, **12**, 151 (1935); *Brit. Chem. Abs.*, **1935A**, 832.

⁸⁷ Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

⁸⁸ Ayyar, P. R., *J. Indian Inst. Sci.*, **18A**, 123 (1935); *Chem. Abs.*, **30**, 2185 (1936).

⁸⁹ West, H. D., and Carter, H. E., *J. Biol. Chem.*, **119**, 103 (1937).

⁹⁰ Haerdi, W., and Thorpe, J. F., *J. Chem. Soc.*, **127**, 1237 (1925).

⁹¹ Nicolet, B. H., and Sattler, L., *J. Am. Chem. Soc.*, **49**, 2069 (1927).

cyclopropane-1,1-dicarboxylate even in diffused light. The nature of the product depended on the conditions of bromination. Apparently both ethyl 2-bromocyclopropane-1,1-dicarboxylate and β -bromoethylbromomalonate were formed in all cases, but the proportion of the latter was much higher when the bromination was carried out at higher temperatures and under mercury-arc illumination. The former is apparently the primary product from which the latter is produced by subsequent reaction of the hydrobromic acid liberated. Bromination of cyclopropane-1,1-dicarboxylic acid in carbon tetrachloride in ultraviolet light affords bromo- β -bromoethylmalonic acid. In chloroform, the product is a viscous oil, which loses carbon dioxide upon distillation with the formation of 2-bromocyclopropane-carboxylic acid. Bromination of ethyl 1-cyanocyclopropane-1-carboxylate affords ethyl 2-bromo-1-cyanocyclopropane-1-carboxylate and ethyl α,γ -dibromo- α -cyanobutyrate. Bromine is without action in ultraviolet light on cyanocyclopropane and 1-cyanocyclopropane-1-carboxylic acid.

The photobromination of cyclohexane by rays of wave-length 5460A at 30°C. has been investigated by Wood and Rideal.⁹² Both the thermal and the photochemical reactions conform to the unimolecular law and the latter has no temperature coefficient. The velocity of the reaction is proportional to the light intensity, independent of the cyclohexane concentration and reduced by the presence of oxygen, the inhibition by the latter being independent of the pressure of the cyclohexane. Jost⁹³ found the characteristics of the reaction to be the same in both the regions of continuous and discontinuous absorption by the halogen. The reaction constant varied approximately with the square root of the cyclohexane concentration. The temperature coefficient was two and the quantum yields increased with rising temperatures.

In carbon tetrachloride, the chlorination of this compound under the influence of either white or monochromatic light, is unimolecular with respect to chlorine. The velocity coefficient is directly proportional to the intensity of the incident radiation, independent of the concentration of chlorine and increases slightly with the concentration of the cyclohexane.⁹⁴ The coefficient diminishes a little as the reaction proceeds, apparently because of the retarding influence of the chlorocyclohexane formed. The quantum efficiency is 19 at 4360A, 30 at 4040A and 41 at 3660A. The temperature coefficients for these wave-lengths are 1.5, 1.29 and 1.26, respectively.

AROMATIC COMPOUNDS

The influence of light in facilitating the chlorination of toluene in the side-chain has long been known and employed in practice. Before discussing this reaction and its application, attention will be devoted to the halogenation reactions of benzene.

Luther and Goldberg⁹⁵ found the frequently irregular course of the photochlorination of benzene to be due to the retarding effect of small quantities of oxygen, an effect frequently noted in chlorination reactions in general. The rate of the reaction with liquid benzene is proportional to the square of the pressure of the chlorine employed. The final product seems to be largely benzene hexachloride.⁹⁶

On the other hand, in the vapor phase the reaction proceeds by a *short-chain*

⁹² Wood, B. J., and Rideal, E. K., *J. Chem. Soc.*, 2466 (1927).

⁹³ Jost, W., *Z. physik. Chem., Bodenstein Festschrift*, 291 (1931).

⁹⁴ Basu, K. P., *J. Indian Chem. Soc.*, **6**, 691 (1929); *Chem. Abs.*, **24**, 1033 (1930).

⁹⁵ Luther, R., and Goldberg, E., *Z. physik. Chem.*, **56**, 43 (1906); *J. Chem. Soc.*, **90**, (II), 641 (1906).

⁹⁶ Slatov, A., *Z. physik. Chem.*, **45**, 540 (1903).

mechanism.⁹⁷ It was found that the main initial reaction is one of addition but that some substitution also occurs. At the beginning, the rate of change of pressure is proportional to the square root of the light intensity and to the pressure of the chlorine and that of the benzene. No pressure change is observed unless phenyl chloride forms and condenses on the wall. After this there is a liquid reaction which consists in large part in the addition of chlorine to benzene dissolved in the liquefied phenyl chloride.

In the gas phase photochlorination of chlorobenzene, which also proceeds by short chains, the initial rate of reaction of the chlorine is proportional to a power of the light intensity between 0.5 and 1.0. The rate is also about proportional to the product of the chlorine and chlorobenzene concentrations and is increased by surfaces. The ratio of substitution to addition increases from much less than one to more than one as the ratio of chlorine used to the initial pressure of chlorobenzene increases. The rate of addition of chlorine to *p*-dichlorobenzene is slightly less than that to chlorobenzene. Some intermediate substances have been isolated; the final product is dodecachlorocyclohexane.

There is little difference in the rates of photochemical chlorination of the three dichlorobenzenes.⁹⁸ The rate is proportional to the light intensity at low intensities but at higher ones depends on some power between 0.5 and 1.0. It is independent of the chlorine pressure except as this affects the light absorption, but is proportional to the pressure of dichlorobenzene.

The rate of addition of liquid chlorine to three trichlorobenzenes in sunlight at room temperature has been found by van der Linden⁹⁹ to decrease in the order of the 1,2,3-, 1,2,4- and 1,3,5- compounds, requiring 7 days, 10 days and 9 weeks, respectively. The first gives only one isomer of 1,1',2,2',3,3',4,5,6-nonachlorocyclohexane, of musty camphor-like odor, m.p. 80°C. The second gives a series of mixed crystals of two isomers of $C_6H_3Cl_9$ and 1,2,2',3,4,4',5,6-octachloro-6-cyclohexene, obtained by the loss of hydrogen chloride from a third unstable isomer. The 1,3,5-trichlorobenzene yields one isomer of 1,1',2,3,3',4,5,5',6-nonachlorocyclohexane. Addition is assumed to occur most readily at double linkings unsubstituted in both Kekule forms. Van der Linden also reports¹⁰⁰ on the addition of chlorine to penta- and hexachlorobenzene. The former yielded hexachlorobenzene and a mixture of 1,2,3,3',4,4',5,6,6'-*cnn*eachloro-1-cyclohexene and its stereoisomer. The hexachlorobenzene gave dodecachlorocyclohexane and a small quantity of decachlorocyclohexene.

The β -isomer of hexachlorobenzene after 17 days in sunlight, formed principally β -*p*-dichlorobenzene hexachloride and probably the 1,2,4-trichlorine derivative.¹⁰¹

Hexabromodihydrobenzene and liquid chlorine, exposed to sunlight for 40 days in a sealed tube, gave dodecachlorohexane, $C_6H_2Cl_{12}$, melting 108-110°C.¹⁰²

The liquid phase photobromination of benzene in carbon tetrachloride by low concentrations of bromine (1 to 2 mg. per cc.) has been studied by Meidinger.¹⁰³ The bromine can either be directly substituted in the ring with the formation of monobromobenzene, or the double bonds may be broken with the formation of

⁹⁷ Lane, C. E., Jr., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 161 (1932); Smith, H. P., Noyes, W. A., Jr., and Hart, E. J., *Ibid.*, **55**, 4444 (1933); Hart, E. J., and Noyes, W. A., Jr., *Ibid.*, **56**, 1305 (1934).

⁹⁸ Fisk, C. F., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1707 (1936).

⁹⁹ van der Linden, T., *Rec. trav. chim.*, **55**, 315 (1936); *Chem. Abs.*, **30**, 6345 (1936).

¹⁰⁰ van der Linden, T., *Rec. trav. chim.*, **55**, 569 (1936); *Chem. Abs.*, **30**, 7103 (1936).

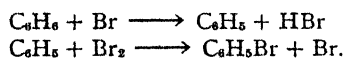
¹⁰¹ van der Linden, T., *Rec. trav. chim.*, **57**, 217 (1938); *Chem. Abs.*, **32**, 4542 (1938).

¹⁰² van der Linden, T., *Ibid.*, **57**, 401 (1938); *Chem. Abs.*, **32**, 5775 (1938).

¹⁰³ Meidinger, W., *Z. physik. Chem.*, **5B**, 29 (1929); *Z. Elektrochem.*, **35**, 738 (1939).

benzene hexabromide. The reaction is independent of the bromine concentration and of the wave-length of light used. Meidinger was unable to explain his observation that the temperature coefficient decreased from 1.6 to 1.0 as the concentration of benzene employed decreased.

Rabinowitsch¹⁰⁴ also found the temperature coefficient 1.6; it varied but little with the light intensity or the wave-length between 3000 and 5500 Å. There was, however, a fall with wave-lengths approaching the convergence limit of bromine and an increase with increasing concentrations of the latter. The quantum yield at room temperature was 0.4 to 0.9. This author believed that even when the solution was considerably diluted with solvent, the bromine molecules remained attached to the benzene molecules and on light absorption reacted with them. The compound $C_6H_6Br_6$ may be formed chiefly by the reaction of activated bromine molecules, but the phenyl bromide results from a reaction with bromine atoms:



The first of these requires thermal activation and accounts for the high temperature coefficient of the photochemical reaction and the lessening of the coefficient on dilution.

In a sealed tube exposed to light, phenyl fluoride and liquid chlorine react vigorously, yielding in a day a few crystals, possibly 1-fluoro-1,2,3,4,4',5,6-heptachlorocyclohexane¹⁰⁵ and an oil which on steam distillation yielded a volatile oil, $C_6H_5FCl_6$, and a non-volatile residue, probably a mixture of isomers of this composition. Under similar conditions, phenyl bromide liberated bromine and hydrogen chloride and formed a chlorobromobenzene hexachloride. Phenyl iodide reacted much more slowly; among the products isolated after several weeks were C_6ICl_5 , $p\text{-ClC}_6H_4I$ and probably 2,4,5-trichloriodobenzene.

Toluene. According to Book and Eggert,¹⁰⁶ toluene, chlorinated by a stream of chlorine at 105° to 110°C., yields almost exclusively benzyl chloride, irrespective of whether the reaction is carried out in light or in darkness, provided a chlorine "carrier," *e.g.*, ferric chloride, is not present. In the presence of such a "carrier," however, considerable amounts of *o*- and *p*-chlorotoluene are produced. At -80°C. a photochemical reaction occurs in the absence of a carrier as a result of absorption of the orange and light green mercury lines, with a quantum yield of about 25. The initial reaction probably comprises the formation of hydrogen chloride together with chlorotoluene or benzyl chloride.

The influence of light on the chlorination of toluene has been the subject of several early patents.¹⁰⁷

In the laboratory of the senior author,¹⁰⁸ a number of experiments have been made to compare the production of benzyl chloride, benzal chloride and benzotrichloride under various conditions. The best results were obtained by passing an excess of toluene vapor mixed with chlorine through a transparent quartz tube at variously elevated temperatures and exposed to ultraviolet radiations. The product was withdrawn from the reaction tube and the contents collected and fractionated; the unused toluene was returned through the reaction tube. In order to determine the effect

¹⁰⁴ Rabinowitsch, E., *Z. physik. Chem.*, **19B**, 190 (1933).

¹⁰⁵ van der Linden, T., *Rec. trav. chim.*, **55**, 282 (1936); *Chem. Abs.*, **30**, 5192 (1936).

¹⁰⁶ Book, G., and Eggert, J., *Z. Elektrochem.*, **29**, 521 (1923); *Ber.*, **59B**, 1192 (1926); *Chem. Abs.*, **18**, 668 (1924); See also Bergel, F., *Ber.*, **59B**, 153 (1926); *Chem. Abs.*, **20**, 1602 (1926).

¹⁰⁷ See, *e.g.*, Ransford, R. B., *British P.* 16,317, July 8, 1914; *J. Soc. Chem. Ind.*, 1203 (1915).

¹⁰⁸ Ellis, Carleton, U. S. P. 1,202,040, Oct. 24, 1916; for a special form of chlorination chamber, Ellis, Carleton, U. S. P. 1,146,142, July 13, 1915.

of ultraviolet rays on this reaction the source of the rays was removed and the experiment carried out in a similar manner. The results of one test are given in Table 22.

Table 22.—Products from Chlorination of Toluene.

Fraction	Quartz Tube without Ultraviolet	Quartz Tube with Ultraviolet
	per cent	
Up to 150°C.	72	42
150-170°C.	4.2	2.
170-185°C.	18.5	47.5
185-215°C.	3.8	6.5

A process for the manufacture of side-chain chlorinated toluene advocated by Gibbs and Geiger,¹⁰⁹ called for ultraviolet radiation. It was claimed that when toluene in vapor phase is mixed with chlorine gas in the definite theoretical proportions to produce chlorinated side-chain products and the mixture exposed to ultraviolet rays, the bodies desired are produced in greatly increased yields and without the production of interfering by-products. By carefully regulating the speed at which the reacting substances pass continuously through the reaction chamber, a high degree of purity results. They state that it is advisable to work without a catalyst since it is not essential to the reaction and would tend to contaminate the products. According to this process, benzyl chloride, benzal chloride and benzotrichloride may be produced in accordance with the proportion of chlorine employed. Gibbs¹¹⁰ states that when a low-pressure mercury-vapor lamp is used, a mixture of benzyl chloride and benzal chloride is produced and that a high-pressure mercury-vapor lamp gives benzotrichloride. Conklin¹¹¹ has patented sectional glass reaction towers for the chlorination of benzene or toluene under the influence of actinic rays. However, the use of ultraviolet rays is not essential.¹¹²

In experiments on the photobromination of toluene, made in atmospheres of 96 per cent and 4 per cent nitrogen, LeBlanc and Andrich¹¹³ found the yield of benzyl bromide independent of the intensity of light and constant throughout the entire portion of the spectrum investigated. The speed of the reaction decreased with decrease of wave-length and was practically zero for wave-lengths shorter than 3000A. Swensson¹¹⁴ reports that the rate of absorption of bromine by toluene and xylene in the presence of alcohol and when exposed to the rays of a quartz mercury arc at 20°C. is retarded, owing to the ability of alcohol to remove the hydrogen bromide, which catalyses the reaction, at the same time being itself decomposed. Kharasch, White and Mayo¹¹⁵ believe that in light the yield of the side-chain bromination reaction is lowered when oxygen is partly excluded. They consider it a chain reaction carried by bromine atoms, the source of which may be hydrogen bromide when oxygen or oxygen carriers are present.

Natelson¹¹⁶ obtained an 85-per cent yield of $C_6H_5CHClCH_3$ based on the

¹⁰⁹ Gibbs, H. D., and Geiger, G. A., U. S. P. 1,246,739, Nov. 13, 1917; Canadian P. 186,466, Sept. 10, 1918.

¹¹⁰ Selden Co. and Gibbs, H. D., British P. 123,341, Oct. 22, 1927; *Chem. Abs.*, **13**, 1478 (1919); *J. Soc. Chem. Ind.*, **38**, 268A (1919).

¹¹¹ Conklin, E. P., U. S. P. 1,828,859, Oct. 27, 1931, to Solvay Process Co., *Chem. Abs.*, **26**, 632 (1932).

¹¹² Silberrad, O., and Boake, A., [British P. 259,329, July 22, 1925; *Chem. Abs.*, **21**, 3370 (1927)] chlorinated organic compounds with sulfuryl chloride in the presence of catalysts such as chlorides of phosphorus, manganese, arsenic, selenium, antimony, bismuth, molybdenum, and the chlorides of iron, sulfur and aluminum. Actinic light may be used.

¹¹³ LeBlanc, M., and Andrich, K., *Z. Elektrochem.*, **20**, 543 (1914)

¹¹⁴ Swensson, T., *Z. wiss. Phot.*, **20**, 206 (1921), *J. Chem. Soc.*, **120**, 11, 291 (1921).

¹¹⁵ Kharasch, M. S., White, P. C., and Mayo, F. R., *J. Org. Chem.*, **3**, 33 (1938).

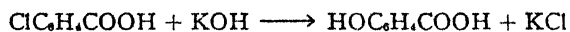
¹¹⁶ Natelson, S., *Ind. Eng. Chem.*, **25**, 1391 (1933).

chlorine employed from ethylbenzene in the light of an S-1 sun-lamp. Evans, Mabbott and Turner¹¹⁷ found chlorination of pure ethylbenzene in diffused daylight to yield a mixture of α - and β -phenylethylchlorides, increased illumination increasing the proportion of the former. In experiments of Varma, Sahay and Subramonium,¹¹⁸ the addition of eight drops of nitrosulfonic acid and two cc. of bromine in ten cc. of acetic acid to ten cc. of ethylbenzene in bright sunlight yielded a small quantity of 4-bromoethylbenzene and four grams of α -bromoethylbenzene. The former product was obtained in greater yield in the absence of light. Bromination of ten cc. of 4-chloroethylbenzene in bright sunlight produced seven cc. of 4-chloro- α -bromoethylbenzene.

Intense visible light causes a rapid reaction between cyclopropane and bromine vapor. About two per cent of the bromine reacted appears as hydrogen bromide. The main product is $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$.¹¹⁹

For the laboratory-scale preparation of *m*-xylylchloride by the chlorination of *m*-xylene with the production of as little 4-chloro-1,3-dimethylbenzene as possible, King and Merriam¹²⁰ developed a chlorinator made from a 500-cc. distilling flask and a Pyrex tube connected to a reflux condenser. It was illuminated by a 400-watt nitrogen-filled lamp while 260 gms. of *m*-xylene was boiled in the flask. Chlorine (126 gm.) was passed in at the rate of 40 gms. per hour through a 0.5 mm. tube directly into the current of vapor. 17 gms. of *m*-xylene was found remaining in the hydrogen chloride absorbers and 305 gms. of product was in the flask. As a result of very careful fractionation, 68.79 gms. of *m*-xylene was recovered and 20.20 gms. of 4-chloro-1,3-dimethylbenzene and 190.83 gms. of *m*-xylyl chloride were obtained. In the presence of oxygen, chlorination was extremely slow.

The influence of ultraviolet radiation, in the presence and absence of catalysts, on the reactivity of halogen bound to a carbon ring, has been investigated by Rosenmund, Luxat and Tiedemann.¹²¹ The comparative inertness of a halogen in an aromatic compound is overcome in the presence of copper at 180 to 220°C. At somewhat lower temperatures, the radiation from a quartz mercury-vapor lamp has a decidedly accelerating effect on the reaction



in the absence of copper and is still more active in its presence. At 104°C., the radiation is still an accelerating agent, but the copper is inactive.

According to Olivier,¹²² when *p*-chlorobenzene sulfochloride in ethereal solution is exposed to direct sunlight or to the rays of a Uviol lamp, chlorine is liberated and oxidation takes place with the formation of the free sulfonic acid. When the experiment is carried out by passing dry oxygen through the ethereal solution of the sulfochloride while exposed to the rays of the lamp, the quantity of chlorine collected shows a deficit when compared with the equivalent of sulfonic acid formed; aldehyde and hydrochloric acid are found in the aqueous liquid on treatment with water. It is probable, therefore, that some of the chlorine reacts with the ether to form chloroethyl ether, which is subsequently hydrolyzed to

¹¹⁷ Evans, E. B., Mabbott, E. E., and Turner, E. E., *J. Chem. Soc.*, 1159 (1927).

¹¹⁸ Varma, P. S., Sahay, V., and Subramonium, B. R., *J. Indian Chem. Soc.*, 14, 157 (1937); *Chem. Abs.*, 31, 7411 (1937).

¹¹⁹ Ogg, R. A., Jr., and Priest, W. J., *J. Am. Chem. Soc.*, 60, 217 (1938).

¹²⁰ King, H. S., and Merriam, M. K., *Proc. Nova Scotian Inst. Sci.*, 18, 276 (1933-4); *Chem. Abs.*, 29, 6214 (1935).

¹²¹ Rosenmund, K. W., Luxat, K., and Tiedemann, W., *Ber.*, 56B, 1950 (1923); *Chem. Abs.*, 17, 4837 (1923).

¹²² Olivier, S. C. J., *Rec. trav. chim.*, 36, 117 (1916); *J. Soc. Chem. Ind.*, 35, 1149 (1916).

aldehyde. Under favorable conditions, the decomposition of the sulfochloride under the influence of light and oxygen amounts to over 40 per cent in six hours, and the reaction is practically inhibited in the absence of light or oxygen and a peroxide may play a part in the reaction. The presence or absence of moisture has no appreciable influence. The photochemical decomposition of the sulfochloride is considerable in ethereal solution but only slight in chloroform. In benzene and carbon tetrachloride, the reaction does not take place. Other sulfochlorides of the benzene series behave in a similar manner but to a lesser degree.

Schmitz and Co.¹²³ have prepared esters of phenol homologs halogenated in the side-chain by treating the esters alone or in suitable solvents, such as carbon tetrachloride, with halogen in the presence of light, especially from a source rich in ultraviolet rays.

Jenkins¹²⁴ employs a 500-watt tungsten lamp in the conversion of ketones of the type $R'.CH_2COR$ and $R.CH_2COR'$ into α -bromo- derivatives such as $R'CHBrCOR$ and $RCHBrCOR'$. Feist¹²⁵ finds that *p*-acetyltoluene in the light of a mercury lamp at 100 to 110°C. adds six atoms of chlorine, forming *p*-trichloroacetyl trichloromethyl benzene. According to Connerade,¹²⁶ the chlorination of dimethylbenzophenone first at 120°C. and then at 140°C., yields, besides products chlorinated in the ring, $(Cl_2CHC_6H_4)_2CO$, a liquid freezing to a crystalline paste at about 0°C. It is very sensitive to light, which transforms it into a plastic mass.

According to I. G. Farbenindustrie,¹²⁷ 2,5-dimethyl-4-chlorobenzophenone may be chlorinated by trichlorobenzene at 170-180°C. while being exposed to the action of a mercury-vapor lamp to give an ω -hexachloro- derivative.

Van der Linden¹²⁸ has obtained, after chlorination of benzoic acid in sunlight, a γ - and a β -hexachloride, a pentachlorocyclohexene carboxylic acid and a mixture which, when distilled in steam, yielded the first two of these, the α -isomer, 1,2,4,5-tetra-, penta- and hexachlorobenzene and pentachlorocyclohexene carboxylic acid.¹²⁹ He found also that benzoyl chloride and chlorine in sunlight slowly gave a mixture of equal parts of δ -1,2,3,4,5,6-hexachlorocyclohexane carboxylchloride and β -1,2,3,4,5,6,4'-heptachlorocyclohexane carboxylchloride, a γ -isomer of the δ -compound, an α -isomer of the β -compound and an oil which, after treatment with dilute alkali and steam distillation yielded a little 1,2,4,5-tetrachlorobenzene, three isomeric hexachlorocyclohexenes, a mixture of $C_6H_4Cl_2COOH$ and $HOC_6H_4Cl_6COOH$ or of $HOC_6H_5Cl_5COOH$ and $C_6H_5Cl_6COOH$, the acid of the δ -carboxylchloride and ϵ -benzoic acid hexachloride.

Perkin and Stone¹³⁰ find that when 2,4-dimethyl benzoyl chloride is brominated at 160°C. by the aid of a mercury lamp, the bromo-acid bromide distilling at 169-171°C. at 15 mm., consists mainly of 2-bromomethyl 4-methyl benzoylbromide, $CH_3C_6H_3(CH_2Br)COBr$, but the fraction 160-180°C. at 15 mm., contains this substance and 4-bromomethyl 2-methylbenzoyl bromide, $CH_2BrC_6H_3CH_3COBr$, in the proportion of about 85 to 15 per cent. When 2,4-dimethylbenzoyl chloride is treated with a calculated amount of chlorine for the introduction of three atoms, at a temperature rising from 180 to 210°C. and in ultraviolet light, and the product is distilled, a fraction is obtained boiling 184-186°C. (16 mm.), the

¹²³ British P. 3053, Feb. 5, 1914, to Schmitz and Co.

¹²⁴ Jenkins, S. S., *J. Am. Chem. Soc.*, **56**, 682 (1934).

¹²⁵ Feist, F., *Ber.*, **67B**, 938 (1934).

¹²⁶ Connerade, E., *Bull. soc. chim. Belg.*, **43**, 447 (1934); *Chem. Abs.*, **29**, 768 (1935).

¹²⁷ British P. 394,990, June 29, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **28**, 176 (1934).

¹²⁸ van der Linden, T., *Rec. trav. chim.*, **53**, 703, 779 (1934); *Chem. Abs.*, **28**, 5425 (1934).

¹²⁹ See also for the chlorination of aromatic carboxylic acids in sunlight, Feist, F., German P. 563,129, May 21, 1930, to I. G. Farbenind. A.-G.

¹³⁰ Perkin, W. H., Jr., and Stone, J. F. S., *J. Chem. Soc.*, **127**, 2275 (1925).

chlorine content of which corresponds to that of the expected ω -trichloro-2,4-dimethyl benzoyl chloride. It was found, however, that this fraction was in reality an almost constant boiling mixture of di- and tetra-chlorinated dimethylbenzoyl chloride. When the chlorination was continued in ultraviolet light until the increased weight corresponded to the introduction of four atoms of chlorine, and the product fractionated, 2,4-di(dichloromethyl)benzoyl chloride, boiling at 192-193°C. (10 mm.) was obtained in good yield. An acid chloride fraction boiling 188-192°C. (14 mm.) was obtained when chlorine was passed into 2,4-dimethyl benzoyl chloride in the presence of ultraviolet light at 200°C. until the increase in weight corresponded to the absorption of five atoms of chlorine. The product contained about equal quantities of the isomeric chlorides, $\text{CCl}_3\text{C}_6\text{H}_3$ (CHCl_2) COCl and $\text{CHCl}_2(\text{CCl}_3)\text{COCl}$. It was also possible to obtain the chloride of 2,4-di(trichloromethyl)benzoic acid by chlorinating at 220°C. in ultraviolet light until six chlorine atoms were absorbed. The yield was 70 to 80 per cent.

The bromination of salicyclic acid to the dibromo- derivative occurs slowly in carbon tetrachloride either in daylight or darkness, and more rapidly in methyl alcohol; but exposure to daylight or to the light of a mercury-vapor lamp scarcely accelerates the reaction.¹³¹

Austin and Bousquet¹³² cause phthalide to react with a rapid flow of chlorine in ultraviolet light at 130-140°C. with vigorous agitation, until approximately 0.75 atom of chlorine per molecule is absorbed. The chlorination product, on hydrolysis with boiling water, followed by cooling, filtering and recrystallizing from benzene, yields phthaldehydic acid. Similarly, a 5-nitro- acid may be formed from 5-nitrophthalide.

Matthews, Bliss and Elder¹³³ have found that styrolene may be prepared from β -bromohydrocinnamic acid by the action of steam, by a silent electric discharge or by ultraviolet rays.

In the bromination of stilbene in carbon tetrachloride, the velocity coefficient is independent of the concentration of the bromine, but increases as the initial concentration of the stilbene increases. The temperature coefficient is 2.6. The quantum yield is 305 molecules of stilbene dibromide per absorbed quantum.¹³⁴

In direct sunlight or artificial light (but not in darkness in the absence of peroxidic substances), a solution of isostilbene in benzene is transformed by the action of hydrogen bromide into stilbene in about five minutes. The reaction is prevented by antioxidants. It cannot be effected by the use of hydrogen chloride.¹³⁵

According to Ghosh and Basu,¹³⁶ the photobromination of ethyl *m*-nitrobenzylidene malonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light. A rise in temperature causes a slight increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentration of ester, bromine or dibromide. With Bhattacharya, these authors¹³⁷ found an analogous behavior in carbon disulfide, but the values for the equilibrium constant were but one-seventh of those

¹³¹ Kaufmann, H. P., and Hansen-Schmidy, E., *Archiv Pharm.*, **263**, 32 (1925).

¹³² Austin, P. R., and Bousquet, E. W., U. S. P. 2,047,946, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, **30**, 6011 (1936); *Brit. Chem. Abs.*, **B**, 879 (1937).

¹³³ Matthews, F. E., Bliss, H. J. W., and Elder, H. M., *British P.* 16,828, July 22, 1913.

¹³⁴ Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2**, 261 (1925); **4**, 553 (1927); *Chem. Abs.*, **20**, 1953 (1926); **22**, 4379 (1928). See also Kato, S., *Bull. Inst. Phys.-Chem. Research (Tokyo)*, **11**, 765 (1932); *Chem. Abs.*, **26**, 5260 (1932). Quite different results have been reported by Berthoud¹³⁵ and coworkers.

¹³⁵ Kharasch, M. S., Mansfield, J. V., and Mayo, F. R., *J. Am. Chem. Soc.*, **59**, 1155 (1937).

¹³⁶ Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **4**, 375 (1927); *Brit. Chem. Abs.*, **1928 A1**, 176.

¹³⁷ Bhattacharya, S. C., Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **5**, 183 (1928); *Brit. Chem. Abs.*, **1928A**, **11**, 757.

in the former solvent. The velocity of the initial stage was proportional to the concentration of bromine and increased considerably with increase in concentration of the ester.

The rate of the addition in chloroform, measured under conditions in which the back reaction is negligible, follows the same laws as the photobromination of cinnamic acid and stilbene.¹³⁸

Tetrachloroarsine, RAsX_4 , was found by Hamilton and King¹³⁹ to decompose into RX and AsX_3 under the influence of ultraviolet light at temperatures of 75 to 120°C. At temperatures around 100°C. the orange-colored 4-methyl phenyl-tetrachloroarsine suddenly decomposed into *p*-chlorotoluene and arsenic trichloride after having been exposed to the radiations for about two hours. With continued chlorination at the same temperature and in the presence of ultraviolet light, there was a rapid gain in weight, indicating that the *p*-chlorotoluene was being chlorinated. Use may be made of the ability of ultraviolet light to break an arsenic-to-carbon linkage in determination of the structure of more complex arsenicals. It was found in the case of *p*-toluene arsenic acid that chlorine substituted in the nucleus and not in the sidechain. In order to prove the position of the chlorine in the ring the arsenic acid was converted into the corresponding tetrachloroarsine, the arsenic-to-carbon linkage broken by the action of chlorine under the influence of ultraviolet light, and the dichlorotoluene thus formed was chlorinated and hydrolyzed to yield 2,4-dichlorobenzoic acid.

HALOGENATION OF OTHER TYPES OF COMPOUNDS

Ultraviolet light has been suggested as an aid in the preparation of chloronaphthalene.¹⁴⁰ According to Davies and Oxford,¹⁴¹ 4,1-nitromethyl naphthalene and bromine when exposed in a quartz flask to ultraviolet light give a yellow monobromo- derivative, melting at 137.5 to 138.5°C and a very small quantity of a tetrabromo- derivative, melting at 189 to 190°C. The bromination of naphthalene is a unimolecular reaction having a temperature coefficient of 1.57 per ten degrees between 5 and 30°C., according to Kozak and Pazdor.¹⁴² The velocity for a given rate of absorption of energy is greatest in blue light. The velocity of photobromination of various methyl and ethyl derivatives of naphthalene has also a maximum in blue light, but with the bromine substitution reactions of these substances, and also of toluene, there is a secondary maximum in the yellow range.

1,5-dibenzoyl-2,6-dimethyl, 1,5-di(*o*-chlorobenzoyl) and 1,5-di(2,5-dichlorobenzoyl)-2,6-dichloronaphthalene are chlorinated at from 160 to 200°C. with a finely divided stream of chlorine in the light of a mercury lamp to give the ω -hexachloro- derivative. The products are condensed by treatment with concentrated sulfuric acid.¹⁴³

Chlorination of 2-methyl- α -naphthoyl chloride at 150 to 170°C. under the influence of arc lamp irradiation, and hydrolysis of the resulting product with water and calcium carbonate forms β -naphthylaldehyde-1-carboxylic acid.¹⁴⁴

¹³⁸ Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

¹³⁹ Hamilton, C. S., and King, W. N., *J. Am. Chem. Soc.*, **55**, 1689 (1933).

¹⁴⁰ Ellis, C., and McElroy, K. P., U. S. P. 914,251, March 2, 1909; *Chem. Abs.*, **3**, 1447 (1909).

¹⁴¹ Davies, J. S. H., and Oxford, A. E., *J. Chem. Soc.*, 220 (1931).

¹⁴² Kozak, J., and Pazdor, F., *Bull. Akad. Polonaise*, **A**, 477, 489 (1933); *Chem. Abs.*, **28**, 4114 (1934).

¹⁴³ British P. 427,327, April 23, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **29**, 5866 (1935).

¹⁴⁴ Mayer, F., Schafer, W., and Rosenbach, J., *Arch. Pharm.*, **267**, 571 (1929); *Brit. Chem. Abs.*, **1928 A**, 1294.

Tatum and Thomson¹⁴⁵ prepare α -halogenated anthraquinones by halogenating in the sun, or other actinic light, anthraquinone or its halogenated derivatives capable of further α -halogenation, in the presence or absence of halogen carriers, solvents or diluents. Thus anthraquinone is chlorinated in oleum in the presence of iodine under the action of sunlight, 1,4,5,8-tetrachloroanthraquinone being obtained. This, treated with phthalimide, and hydrolyzed to the tetra-amino-derivative, yields dyes which turn blue.

Phenanthrene can be brominated only by a light reaction.¹⁴⁶

Terpenes. Cineole, in carbon tetrachloride solution, has been chlorinated in sunlight by Gandini,¹⁴⁷ who obtained a mono- and a di-chloro- derivative. Although light is indispensable for the formation of the mono-chloro- derivative, the reaction is slower and the yields are lower in ultraviolet light. In later work,¹⁴⁸ there was obtained from 100 gms. of cineole, 15 gms. of a mixture of 2-chlorocineole and 3-chlorocineole, 80 gms. of dichloroisomers, 25 gms. of a trichloro- derivative and 25 gms. of undistilled residue. A still higher percentage of chlorine led to more extensive chlorination and to products which could not be separated. Separation of the dichloroisomers yielded 2,3-dichlorocineole, an oil which slowly turns pale yellow on exposure to light.

Passage of chlorine into cumene containing 15 per cent acetic acid in sunlight affords *p*-chlorocumene and 1,3-dichloro-2-phenylpropane, the relative yields depending on the light intensity.¹⁴⁹

Pseudocumene can be brominated by mixing with bromine and exposing to sunlight for about three hours.¹⁵⁰ The products formed depend upon the nature of the subsequent heating. If the exposed mixture is heated on a water-bath only the monobromide is obtained, but if it is heated to 170°C., a mixture of mono-, di- and tribromides results; the relative proportions depend upon the amount of bromine used. A mixture of 5-bromopseudocumene and bromine exposed to sunlight for three hours and heated for three hours gave di- and tri-nuclear substituted bromine derivatives in fairly good yields. In Bruylants's method for the preparation of trimethylene chlorobromide, allyl chloride is saturated with hydrobromic acid in sunlight. Strukov¹⁵¹ finds the yield 95-97 per cent.

In direct sunlight in chloroform, camphane reacts immediately with chlorine with evolution of hydrogen chloride. The product yields bornyl chloride, which, treated in direct sunlight with chlorine in ice-cold carbon tetrachloride, yields a mixture of various halogenated derivatives difficult to separate. Gandini¹⁵² was able to obtain 2,3-dichlorocamphane, melting at 126-126.5°C., a trichloro- derivative, melting at 130-2°C., and other unidentified compounds.

Diphenosuccindan-9,12-dione in carbon tetrachloride may be brominated in the light of an arc lamp to the 10-bromo- compound.¹⁵³

Light has no influence on the chlorination of lignin.¹⁵⁴ On the other hand, chlorination of wool is slower in diffused light than in direct light.¹⁵⁵

¹⁴⁵ Tatum, W. W., and Thomson, R. F., *British P.* 364,141, Sept. 2, 1930; *Chem. Abs.*, **27**, 1640 (1933).

¹⁴⁶ Kharasch, M. S., White, P. C., and Mayo, F. R., *J. Org. Chem.*, **2**, 574 (1938).

¹⁴⁷ Gandini, A., *Gazz. chim. ital.*, **63**, 151 (1933); *Chem. Abs.*, **27**, 3707 (1933).

¹⁴⁸ Gandini, A., *Gazz. chim. ital.*, **64**, 118 (1934); *Chem. Abs.*, **28**, 4723 (1934).

¹⁴⁹ Varma, P. S., and Srinivasan, M. K., *J. Indian Chem. Soc.*, **13**, 189 (1936); *Chem. Abs.*, **30**, 5949 (1936); see also Qvist, W., and Salo, A., *Acta Acad. Aboensis, Math. Phys.*, **8**, 4 (1934); *Chem. Abs.*, **29**, 6884 (1935).

¹⁵⁰ Varma, P. S., and Sen-Gupta, D. N., *J. Indian Chem. Soc.*, **11**, 351 (1934); *Chem. Abs.*, **28**, 6119 (1934).

¹⁵¹ Strukov, I., *Khim. Farm. Prom.*, **2**, 66 (1933); *Brit. Chem. Abs.*, **A**, 55 (1934).

¹⁵² Gandini, A., *Gazz. chim. ital.*, **66**, 357 (1936); *Chem. Abs.*, **31**, 2595 (1937).

¹⁵³ Brand, K., Gabel, W., Ott, H., Müller, K., and Fleischbauer, R., *Ber.*, **69B**, 2504 (1936).

¹⁵⁴ Sarkar, P. B., *J. Indian Chem. Soc.*, **11**, 777 (1934); *Chem. Abs.*, **29**, 2514 (1935).

¹⁵⁵ Uetaka, S., *Reports Imp. Ind. Research Inst. Osaka, Japan*, **15**, 11 (1935); *Chem. Abs.*, **29**, 2751 (1935).

Part III

Applications of Photochemistry to Industrial Products

Chapter 29

Reactions of Fatty Acids. The Preservation of Foods

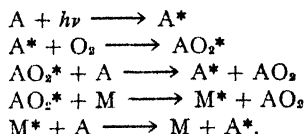
In discussing the effects of light on the production of rancidity in foods, attention is first directed to the photochemistry of the fatty acids since these, when present as esters in fats and oils, are primarily responsible for the changes which occur.

It has been reported that acids with carbon chains longer than C_{12} , both saturated and unsaturated, become ketonic on exposure to light, atmospheric oxygen favoring the reaction.¹ The passage of air in the presence of tropical sunlight through solutions of potassium stearate, palmitate or oleate, according to Palit and Dhar,² is accompanied by oxidation, which increases with the intensity of the light. Zinc oxide is an effective photosensitizer.

The rate of oxygen consumption by undecenic acid, decenic acid, oleic acid and olive oil in light is greatly increased by the addition of very dilute solutions of chlorophyll or eosin as sensitizers, the former being ten times as effective as the latter. Hemin does not act as a sensitizer, at least for the oxidation of decenic and undecenic acids.³ In the case of oleic acid, hydroxyoleic acid is formed. In general, there seemed to be no destruction of double bonds in these experiments.

Täufel and Seuss⁴ found that the oxygen absorption, peroxide formation and epihydrinaldehyde formation in a highly purified sample of oleic acid was affected by light in the same manner as by the addition in darkness of such catalysts as ferrous, ferric or cupric chlorides. Custis⁵ found the hydrogenation of oleic acid to be unaffected by ultraviolet radiations from an iron arc. A copper-egg white complex also catalyzes the oxidation of unsaturated fatty acids; this effect may be increased five to ten times by irradiation of the complex.⁶

Linoleic acid takes up oxygen and forms peroxides by a photochemical chain reaction.⁷ The rate of peroxide formation is independent of the oxygen concentration and temperature and proportional to the concentration of acid and to the square root of the light intensity. As steps in the mechanism the following reactions were suggested (A is linoleic acid and M solvent):



¹ Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine Ind.*, **26**, 3, 87 (1933); *Brit. Chem. Abs.*, **B**, 416 (1935).

² Palit, C. C., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1263 (1928).

³ Meyer, K., *J. Biol. Chem.*, **103**, 597 (1933). Certain porphyrins also inhibit the autoxidation of a mixture of linoleic and linolenic acids in sodium cholate solutions at pH 7.12. The inhibitors may be destroyed by ultraviolet irradiation. Hinsberg, K., and Ammon, R., *Z. physiol. Chem.*, **246**, 139 (1937).

⁴ Täufel, K., and Seuss, A., *Fettechem. Umschau*, **41**, 107, 131 (1934); *Chem. Abs.*, **29**, 370 (1935).

⁵ Custis, H. H., *J. Frank. Inst.*, **184**, 880 (1917).

⁶ Kather, E., *Arch. exp. Path. Pharmacol.*, **184**, 645 (1937); *Chem. Abs.*, **32**, 8448 (1938).

⁷ Horio, M., *Mém. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 18, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934); Horio, M., and Monden, S., *J. Soc. Chem. Ind. Japan*, **37**, 488B (1934); *Chem. Abs.*, **29**, 52 (1935); Horio, M., and Yamashita, S., *J. Soc. Chem. Ind. Japan*, **37**, 392, 416 (1934); *Chem. Abs.*, **28**, 7165 (1934).

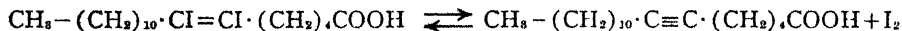
Light rays shorter than 4000Å are effective, ordinary sunlight having only a few suitable wave-lengths for oxidative action.

These observers also found that in the absence of oxygen the light of a mercury arc caused a bleaching of mixtures of aqueous solutions of linoleic acid with alcoholic solutions of eosin, Victoria Violet or erythrosin (but not Victoria Blue, which is non-fluorescent) more rapid than in darkness. The dye is reduced and the acid oxidized. The bleaching of the dye was less rapid when oxygen was bubbled through the solutions.

The rate of bromination of oleic, linoleic and linolenic acids is in inverse ratio to the number of double bonds they contain,⁸ oleic acid acting the most and linolenic acid the least rapidly. Under the influence of ultraviolet light the bromination of both the so-called "pure" acids and the mixed fatty acids proceeds further than in darkness. This was held to indicate the presence of unsaturated isomers not revealed by the usual analytical methods.

As in the case of other unsaturated compounds, stereoisomeric transformations and polymerization reactions occur during irradiation. The former have been relatively little studied; the latter are discussed particularly in the following chapter.

Irradiation of "iodostarin" (di-iodide of tariric acid) in chloroform by sunlight, mercury-vapor light or Osram light, causes its dissociation into tariric acid and iodine.⁹



At room temperatures, the change is reversible and follows the law of mass action, but at higher temperatures there are deviations from this behavior. The equilibrium is independent of the strength of the light, but the rates of reaction are directly proportional to it. Since it was found that this decomposition is caused by the rays absorbed by the iodine, the photolysis must be regarded as sensitized by iodine.

Ultraviolet light promotes the formation of a diricinoleic acid by the condensation of the hydroxyl group of one molecule of ricinoleic acid with the carboxyl group of another.¹⁰

Lederer¹¹ investigated the effect of small concentrations of metals on the color of a two-to-one mixture of stearic and oleic acids in darkness, after eight hours in direct sunlight and after two hours of exposure at 40 cm. from an ultraviolet source. During neither of these exposures did manganese, aluminum, zinc or lead produce a color change. The presence of 0.04 per cent nickel led to a slight yellowing in sunlight but there was no color change after ultraviolet irradiation. Samples with 0.04 per cent copper exhibited distinct yellowing, and those containing iron showed considerable darkening, the effect being more pronounced in sunlight than in ultraviolet light. Samples lacking metallic adulteration were scarcely affected. It was concluded that the discoloration of fats after manufacture is primarily dependent upon the presence of traces of iron and copper.

Triglycerides are said to be hydrolyzed in the presence of water by the action of ultraviolet rays.¹²

⁸ Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.*, **49**, 2808 (1927).

⁹ Baur, E., *Helv. Chim. Acta*, **18**, 1149 (1935); *Chem. Abs.*, **30**, 28 (1936).

¹⁰ Zlatarov, A., and Bieliavski, V., *Ann. univ. Sofia, Faculte phys.-math.*, **28**, No 2, 21 (1932); *Chem. Abs.*, **28**, 3054 (1934).

¹¹ Lederer, E. L., *Z. angew. Chem.*, **42**, 1033 (1929); *Seifensieder Ztg.*, **56**, 278 (1929); *Chem. Abs.*, **24**, 741 (1930).

¹² Tern, R., German P. 357,695; *J. Soc. Chem. Ind.*, **41**, 945A (1922).

DuNoüy¹³ has called attention to a slight decrease in the surface tension of dilute sodium oleate solutions after three hours of exposure to light. Mahajan¹⁴ attributes it to a chemical change which is most marked when ultraviolet light is used. The effect is at a maximum in soap solutions of 6.25×10^{-4} gm. per cc.¹⁵

OILS

Absorption and Fluorescence. The absorption of oils depends upon that of the acids they contain. In the case of cod-liver and other fish oils the well-defined absorption bands are due to sites of unsaturation. The highly absorbing acids obtained from them by saponification are apparently not, however, straight-chain compounds with conjugated double bonds since their absorption may be increased by prolonging the time of the saponification,¹⁶ or by conducting it at elevated temperatures.¹⁷ During this process cyclization probably occurs with the formation of hydroaromatic polycyclic products.

Considerable attention has been devoted to the absorption of fish-liver oils in connection with work on the distribution of vitamins A and D therein. (See Chapter 41.)

Of the vegetable oils studied, linseed oil shows the greatest absorption, according to Harvey,¹⁸ who used an actinometric method which did not permit determination of the wave-length distribution of the absorption. Lewkowitsch¹⁹ measured the absorption of thin films of whale, herring, olive, teaseed and linseed oils. Both the animal and vegetable oils gave curves of the same type, absorption gradually increasing toward the shorter wave-lengths. The feeble absorption bands superposed upon the more or less general absorption could not, however, be used for the purpose of determining individual oils in mixtures. Although Lewkowitsch found in some samples of olive oil indications of a band at 2750A, Lundé, Kringstad and Weedon²⁰ showed that the value of the extinction coefficient at this wave-length characterizes various samples of this oil. In virgin olive oil it was 10 to 22, in refined pressed oil 35-55 and in refined extracted oil 54-90. Two unrefined extracted oils, however, gave values of 80 and 120.²¹

The blue fluorescence follows the same trend. Cortese²² has shown that the examination of the fluorescence of various samples of olive oils cannot distinguish natural (yellow) from refined oil (blue in general), since the addition of chlorophyll or carotene to refined oils imparts to them the fluorescence characteristic of expressed oils. It may be possible to remove this by animal charcoal. Fixed oils from damaged fruit behave like refined oils. Fixed oils from olives stored only two or three days also fluoresce blue-violet.²³

¹³ DuNoüy, P. L., *Nature*, **131**, 689 (1933).

¹⁴ Mahajan, L. D., *Z. Physik*, **98**, 388 (1935).

¹⁵ Acidity developed in a saturated mineral oil when exposed to sunlight or ultraviolet light is believed by Woog, P., [*Compt. rend.*, **189**, 977 (1929)] to affect its spreading on solid surfaces.

¹⁶ Dann, W. J., and Moore, T., *Biochem. J.*, **27**, 1166 (1933).

¹⁷ Edisbury, J. R., Morton, R. A., and Lovern, J. A., *Biochem. J.*, **27**, 1451 (1933); **29**, 899 (1935).

¹⁸ Harvey, E. H., *J. Am. Pharm. Assn.*, **19**, 1173 (1930); **20**, 643 (1931).

¹⁹ Lewkowitsch, E., *J. Soc. Chem. Ind.*, **46**, 195T (1927).

²⁰ Lundé, G., Kringstad, H., and Weedon, H. W., *Angew. Chem.*, **46**, 796 (1933); Kringstad, H., *Angew. Chem.*, **49**, 423 (1936); Moore, T., *Biochem. J.*, **31**, 38 (1937).

²¹ See also Rousscau, E., *Compt. rend. soc. biol.*, **96**, 611 (1927); *Chem. Abs.*, **21**, 1933 (1927).

²² Cortese, D., *Industria chimica*, **9**, 1048 (1934); *Chem. Abs.*, **28**, 7044 (1934); Walter, C., *Olii minerali, olii e grassi, colori e vernici*, **15**, 149 (1935); *Chem. Abs.*, **31**, 6041 (1937); Fachini, S., and Martinenghi, G., *Olii minerali, olii e grassi, colori e vernici*, **17**, 54 (1937); *Chem. Abs.*, **32**, 3647 (1938).

²³ Cusa, W., *Olii minerali, grassi e saponi, colori e vernici*, **18**, 33 (1938); *Chem. Abs.*, **32**, 8178 (1938).

Fluorescence colors excited by ultraviolet light have also been frequently suggested as aids in the identification of other fats and oils. Haitinger, Jorg and Reich²⁴ recorded the fluorescence colors of a number of oils and fats for use in the detection of adulterants in butter, cacao butter, lard, olive oil, etc. Butter is said²⁵ to give a golden yellow color, but margarine and synthetic fats appear grayish white. It is claimed that 20 per cent of foreign fat may easily be detected in this manner. Solid or molten lards²⁶ generally give a slight bluish fluorescence, but no definite conclusions may be drawn from its color as to the origin of the sample. Applied microscopically, the method may be used for distinguishing between shell and nib tissue in cocoa.²⁷ The brilliant white luminescence of cacao butter in the light of a quartz lamp is, according to Mauersberger,²⁸ due to traces of aluminum and calcium soaps formed while in contact with fullers' earth during bleaching. It is not characteristic of extracted butter because any pressed butter similarly treated with fullers' earth would give it.

Much attention has been devoted to the property possessed by seeds and oils of affecting a photographic plate as does light. Stutz, Nelson and Schmutz²⁹ believed it due to the evolution of hydrogen peroxide. The effect is greatly increased by exposure of the oils to light. Since only the unsaturated acids isolated from the oil, and not the saturated ones, are effective, the phenomenon appears to be associated with the drying of the oil. de Loureiro³⁰ attributed the effect to the evolution of ozone. The vapor from the oil must be brought in contact with the photographic plate.³¹ Ried³² believed that the effect in various fats parallels their ability to form vitamin D on irradiation. This has been much discussed, but at present is regarded as merely an incidental phenomenon. Irradiation does not affect the electrical conductivity of cod-liver oil.³³

Photochemical Changes of Various Edible Oils. Wall³⁴ subjected cacao oil to the action of ultraviolet rays to destroy its objectionable taste and odor.

The bleaching of palm oil by light may be sensitized by the addition of various dyestuffs added to aqueous emulsions of the oil. Baur and Fabbriotti³⁵ estimated that the quantum yields when various dyes are employed is low, of the order of 10^{-3} . Exposure of olive oil to ultraviolet radiation for an hour has been found to cause an increase of more than 5 per cent in the acidity.³⁶ After exposure for about a week a comparatively rapid air-drying has been observed.³⁷ During exposure to ultraviolet, radium or x-rays, the dielectric constant, acid number and iodine number are the constants of olive oil which undergo the greatest change.³⁸

Sun rays bleach layers of olive oil from 1 mm. to 1000 mm. in thickness.

²⁴ Haitinger, M., Jorg, H., and Reich, V., *Z. angew. Chem.*, **41**, 815 (1928); Kaufmann, H. P., *Chem. Umschau Fettc, Oele, W'achse, Harze*, **36**, 34 (1929); *Chem. Abs.*, **23**, 2051 (1929); Dérivé, M., *Mat. grasses*, **29**, 246, 279 (1937).

²⁵ Novacek, E., and Hokl, J., *Z. Fleisch. Milchhyg.*, **42**, 47 (1932); *Chem. Abs.*, **26**, 2881 (1932).

²⁶ Braunsdorf, K., *Z. Unters. Lebensm.*, **63**, 407 (1932); *Chem. Abs.*, **27**, 785 (1933).

²⁷ Wasicky, R., and Wimmer, C., *Z. Nahr. Genussm.*, **30**, 25 (1915).

²⁸ Mauersberger, E. A., *Chem. Ztg.*, **56**, 861 (1932).

²⁹ Stutz, G. F. A., Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, **17**, 1138 (1925).

³⁰ de Loureiro, A. J., *Compt. rend. soc. biol.*, **96**, 1321, 1324 (1927); *Chem. Abs.*, **21**, 2484 (1927).

³¹ Hopwood, F. L., and Mayneord, W. V., *Nature*, **116**, 98 (1925).

³² Ried, O., *Wien klin. Woch.*, **42**, 1105 (1929).

³³ Butler, L. W., and Woodrow, J. W., *Iowa State Coll. J. Sci.*, **11**, 333 (1937); *Chem. Abs.*, **32**, 4722 (1938).

³⁴ Wall, E. J., U. S. P. 1,386,476, Aug. 2, 1921; *Chem. Abs.*, **15**, 3913 (1921).

³⁵ Baur, E., and Fabbriotti, G. F., *Helv. Chim. Acta*, **18**, 7 (1935).

³⁶ Lesure, A., *J. pharm. chim.*, **7**, 575; *Chem. Abs.*, **5**, 963 (1911).

³⁷ Eibner, A., and Rasquin, H., *Chem. Umschau*, **33**, 29 (1926); *Chem. Abs.*, **20**, 2422 (1926).

³⁸ Kovalev, T. G., *Izvestiya Zentral. Nauch. Issledovatel'skogo Inst. Pishchevoi Vkhussvoei Prom.*, U.S.S.R., **3**, (1931); *Chem. Abs.*, **26**, 5222 (1932).

but the thicker the layer the slower the action.³⁹ For quick bleaching a maximum contact of oil, air and sunlight is needed. With oil flowing slowly down low steps, bleaching occurs in half the time. The bleaching does not completely destroy the fluorescence observed on exposure of the oil to Wood's light. Thirty days of exposure produced but little change in most of the constants, contrary to the observations of others on the effects of ultraviolet. Thus, the acidity was unchanged, the iodine number increased from 81.9 to 82.8, the refractive index changed from 1.46588 to 1.46625 and the saponification number decreased from 193.5 to 191.9. The density increased from 0.9170 to 0.9175.

Putland⁴⁰ observed a more rapid bleaching of vegetable oils in the light of Mazda lamps than in sunlight. Ultraviolet from a quartz mercury arc, however, darkened instead of bleaching both cottonseed and soybean oils. Crude cottonseed oil, one inch in depth, exposed in a tin tray at 27°C. to the mercury-vapor light, darkened from 35 yellow, 7.9 red (Lovibond scale) in eight hours to 35 yellow, 8.3 red. A bleached cottonseed oil changed in ten hours from 20 yellow, 2.1 red to 20 yellow, 3.0 orange.

In the laboratory of the senior author numerous experiments on the bleaching and polymerization of various oils by a Cooper-Hewitt quartz mercury arc have been made.⁴¹ Samples of crude cottonseed oil, linseed oil, crude whale oil (No. 3) and a strongly fluorescent medium-body lubricating oil were exposed in shallow pans in three-sixteenth inch layers at about eleven inches from the lamp. After three hours the linseed oil had a very heavy film, the cottonseed and whale oils slight films but the lubricating oil was unaltered. After six hours the cottonseed oil had greatly increased in viscosity, the linseed and whale oil had commenced to gelatinize and the lubricating oil had become slightly darker. After 13½ hours, the cottonseed oil had gelatinized and was slightly bleached. The linseed oil had become a stiff jelly and its odor was diminished, but the color was apparently unchanged. The whale oil was considerably deodorized and slightly bleached. The lubricating oil had become somewhat darker, but the fluorescence had completely disappeared.

With exposures closer to the lamp, the whale oil gave a dark, amber-colored jelly with a very faint odor as compared with that of the original oil. Crude cottonseed oil also gave a stiff amber-colored jelly, which was considerably lighter than the original oil. The iodine value had fallen to 56. A highly refined cottonseed oil, however, gave a jelly which in color and consistency could scarcely be distinguished from that of the crude oil. The temperature during irradiation was about 110°C. The crude sample fumed slightly during the exposure to ultraviolet but the refined oil did not fume below 160°C. and then but slightly. Crude oil polymerizes and gelatinizes more rapidly than refined oil. Special experiments in sealed tubes showed that the thickening and polymerization occurs even in the absence of oxygen. In its presence, however, the solidification of unsaturated fatty oils appears to be due jointly to oxidation and polymerization. In one experiment made at a distance of but four inches from the source, a layer of cottonseed oil commenced to thicken immediately and at the end of fourteen minutes had completely solidified to a very thick jelly. A thicker layer (one and a half inches) at four inches from the lamp had become a solid, dark-colored jelly after 7½ hours.

Castor oil after 10½ hours at three inches gave a product identical in appearance and odor with that obtained from cottonseed oil. Red oil (crude oleic acid) fumed slightly at 85°C and copiously at 110°C. A thin surface film appears to protect the under layer from further action until it is removed. When completely solidified it is hard without any tackiness, black and odorless. A highly refined corn oil gave in 14 hours at four inches a jelly of a very light yellow color, the change occurring very gradually. Immediately before the viscous mass commences to solidify, a large number of small bubbles usually appear below the surface and could be still observed even after the oil had become completely solid. In one case a mixture of equal parts of rosin and corn oil became extremely viscous and somewhat darkened after five hours. The carbonizing

³⁹ Loew, G., *Olii minerali, olii grassi, colori vernici*, 12, 89 (1932); *Chem. Abs.*, 26, 6168 (1932).

⁴⁰ Putland, A. W., *Cotton Oil Press*, 7, No. 7, 36 (1923).

⁴¹ Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914. Note also 1,179,414 and 1,180,025.

or discoloring action when very close to the rays was repeatedly noted. It may be partly due to a local superheating of the under layers of the oil.

In one case ordinary cottonseed oil was mixed with 5 per cent of sulfur and exposed to the action of ultraviolet for three hours at 150°C. It remained liquid after treatment. On the other hand, an oil which had been exposed until it was practically at the gelatinization point and then treated with the same amount of sulfur, on further exposure yielded a black, rubber-like solid. Stamberger⁴² stated that vulcanized triolein, which is soluble in acetone and benzene, after treatment with sunlight or ultraviolet light is converted into a solid mass of molecular weight over 7000, insoluble in these and other organic solvents and swelling in benzene. Applications to the making of artificial rubber latex for impregnating textiles and making varnishes have been suggested.⁴³ Ellis also observed that an oil which had been hydrogenated to a titer of 54°C., after an exposure of three hours to ultraviolet light remained unchanged in color, odor and viscosity.

Early attempts to use ultraviolet light in aiding the reaction of catalysts in the hydrogenation of oils do not seem to have been successful.⁴⁴

It has been suggested that the presence of unhydrogenated oils in hydrogenated products may be qualitatively detected by taking advantage of the fact that the former are darkened and polymerized by ultraviolet light while the latter are unaffected. An exposure of several hours is required.⁴⁵

Oxidation of Oils. Much attention has recently been devoted to studies of the oxidation of oils, particularly in regard to the light it throws upon the production of rancidity in foods on storage. Ultraviolet light has a powerful effect upon the susceptibility of cottonseed oil to oxidation.⁴⁶ This change depends, according to Greenbank and Holm,⁴⁷ upon reactions occurring prior to the period of active oxidation.

During the absorption of small quantities of oxygen oxides and peroxides are believed to be formed; these are sometimes termed "moloxydes" of the unsaturated acids. They alter the oxidation-reduction potential in a manner which may be followed by the aid of methylene blue or other indicators. The reduction of this indicator when dissolved in an unsaturated oil is rapid in strong sunlight. By using a 100-watt Mazda lamp as a constant source, the rate of the change in the color of the indicator, followed photoelectrically, affords an indication of the susceptibility of the oil to undergo the changes which lead to rancidity. Horio⁴⁸ measured the rate of the reaction by determining the concentrations of peroxides formed during ultraviolet irradiation of oils while oxygen was bubbled through them. With linseed oil and linoleic acid the rates were independent of the time of irradiation, proportional to the concentration of acid or oil, independent of temperature and oxygen concentration and proportional to the square root of the light intensity. With olive oil, the rate decreased with time to a constant value. The rate-intensity curve for this oil showed a maximum. Certain substances (vanillin, jara-jara, *p*-nitraniline) accelerate the formation of peroxides in ultraviolet light but not in darkness in linseed oil.⁴⁹ Irradiation also accelerates the effects of manganese and lead abietates.

⁴² Stamberger, P., *Rec. trav. chim.*, **46**, 837 (1927); **47**, 973 (1928); Knight, B., and Stamberger, P., *J. Chem. Soc.*, 2794 (1928).

⁴³ Stamberger, P., and Auer, L., British P. 321,693, 1928; *Brit. Chem. Abs.* **B**, 652 (1930).

⁴⁴ Walter, H., *Seifensieder-Ztg.*, **442** (1913); cited by Ellis, C., "Hydrogenation of Organic Substances," 3rd ed., Van Nostrand, 1930; A mercury-sensitized process has been described by Karagunis, G., *Praktika Akad. Athenon*, **11**, 404 (1936); *Chem. Abs.*, **32**, 1580 (1938).

⁴⁵ Ellis, C., and Wells, A. A., *Chem. Engineer.*, **221** (1918).

⁴⁶ Holm, G. E., Greenbank, G. R., and Deysher, E. F., *Ind. Eng. Chem.*, **19**, 156 (1927).

⁴⁷ Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem. Anal. Ed.*, **2**, 9 (1930).

⁴⁸ Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 8 (1934); *Chem. Abs.*, **28**, 5339, 7165 (1934).

⁴⁹ Nakamura, M., *J. Soc. Chem. Ind. Japan*, **40**, 205B, (1937); *Chem. Abs.*, **31**, 6910 (1937).

The velocities of formation of peroxides during irradiation of tung and castor oils are less than those in linseed and tsubaki oils. The peroxides of all these oils are stable at low temperatures in ultraviolet rays.⁵⁰

In the presence of inert gases, olive, peanut, sesame and colza oils were unaffected by ultraviolet light, but in the presence of oxygen there was an increase in density and a decrease in iodine number. The fluorescence changed from yellow to deep blue as the oils became decolorized.⁵¹

Olive, linseed and especially cod-liver oil gain in weight on exposure to air in the absence of light, possibly because of the absorption of oxygen. Preliminary irradiation of the oils by ultraviolet light for thirty hours enhances the rate during fifty days up to a limit beyond which it is decreased. In comparison with the others, cod-liver oil behaves as though it had already been irradiated. The formation of a compound with peroxide oxygen (detected by the liberation of iodine from potassium iodide acidified with acetic acid) shows a relation to the time of irradiation similar to that of the increase in weight.⁵² Peroxides are formed in olive, mustard, cocoanut, Mahua, castor, sesame and linseed oils, butter and some carbohydrates when air is passed through them during exposure to sunlight. In the absence of air, peroxide formation is decreased. All the oil peroxides have the ability to oxidize slowly a solution of glucose at 40°C.⁵³ Fats are believed to form ketones by Schmallfuss, Werner and Gehrke⁵⁴ and saturated and unsaturated acids, glycerol, some esters, soap, beeswax, and cholesterol act similarly. The higher fatty acids are converted to lower acids, and glycerol yields volatile acids. When methyl laurate or glycerol were used, positive aldehyde tests could be obtained.⁵⁵

Soybean oil is rapidly ketonized by light of wave-lengths under 4100A, several times as rapidly as methyl laurate which is appreciably affected only by rays shorter than 3300A.⁵⁶

The prolonged action of ultraviolet light on lard destroys the material causing luminescence, raises the octoic acid value, and forms the substance responsible for the Kreis reaction of rancid fats.⁵⁷ The increase in octoic acid value may be due to pelargonic and azelaic acids formed by oxidation and fission of oleic acid. The substance responsible for luminescence may be a derivative of oleic acid, or of hydroxyoleic acid.

Weak artificial light accelerates the oxidation of beef fat and exposure to direct sunlight for a few minutes suffices to produce rancidity.⁵⁸ The reaction is autocatalytic, even brief exposure to light accelerating the subsequent oxidation. In beef fat, bleaching of the lipochrome occurs at a comparatively early stage of the oxidation process. At least during the early stages, oxidation in the presence of

⁵⁰ Nakamura, M., *J. Soc. Chem. Ind. Japan*, **40**, 229, 230 (1937); *Chem. Abs.*, **31**, 7682 (1937).

⁵¹ Francesconi, L., and Pinoncelli, L., *Ann. chim. applicata*, **24**, 242 (1934); *Chem. Abs.*, **28**, 6006 (1934).

⁵² Delore, P., *Bull. soc. chim. biol.*, **11**, 74 (1929); *Compt. rend. soc. biol.*, **99**, 807 (1928); *Chem. Abs.*, **23**, 724 (1929). See also Zinov'ev, A. A., and Drucker, S. V., *Masloboiho Zhirovoe Delo*, **13**, No. 2, 6 (1937); *Chem. Abs.*, **31**, 7682 (1937).

⁵³ Chacraharti, S. N., and Dhar, N. R., *Indian J. Med. Research*, **17**, 430 (1929); *Chem. Abs.*, **24**, 2166 (1930).

⁵⁴ Schmallfuss, H., Werner, H., and Gehrke, A., *Fettchem Umschau*, **40**, 102 (1933); *Chem. Abs.*, **27**, 3838 (1933).

⁵⁵ Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine-Ind.*, **27**, 79 (1934); *Brit. Chem. Abs.*, **B**, 846 (1936); Lampitt, L. H., and Sylvester, N. D., *Biochem. J.*, **30**, 2237 (1936); *Chem. Abs.*, **31**, 3311 (1937). For a review, see Schmallfuss, H., Werner, H., and Gehrke, A., *Fette u.-Seifen*, **43**, 211, 243 (1936).

⁵⁶ Werner, H., Gehrke, A., and Minkowski, R., *Margarine-Ind.*, **27**, 93 (1934); *Chem. Abs.*, **29**, 7103 (1935).

⁵⁷ Grossfeld, J., *Z. Unters. Lebensm.*, **55**, 376 (1928); *Brit. Chem. Abs.*, **1928B**, 824.

⁵⁸ Lea, C. H., *Proc. Roy. Soc.*, **B108**, 175 (1931).

light has but little effect on the acidity of the fat. There is a distinct parallelism between the intensity of the Kreis reaction (a pink color test with phloroglucinol and hydrochloric acid in a benzene solution) and the active oxygen content of the fat (determined by the liberation of iodine from potassium iodide in acetic acid and chloroform). At low temperatures, however, the content of active oxygen increases more rapidly in a fat than does its ability to respond to the Kreis test. The reverse is true in bright sunlight. The different susceptibilities of various specimens of beef fat to oxidation depends on the chemical nature of the fat itself rather than upon other tissue constituents.

Coe⁵⁹ suggests that under the photosensitizing action of chlorophyll, atomic hydrogen is liberated. This combines with molecular oxygen to form a loosely bound hydrogen peroxide, which unites with the unsaturated bond of the glyceride and produces the rancid compound. The presence of catalase, therefore, is related to its keeping qualities. Other photosensitizers are assumed to be present in animal fats.

Coe and Leclerc⁶⁰ observed that on keeping maize or cottonseed oils in darkness or in green light, high peroxide values may be attained without the usual indications of rancidity being observed. Similar samples exposed to full daylight became rancid in the same period. Those kept in the dark do so on subsequent exposure to light. Lampitt and Sylvester⁶¹ found the Issoglio test useful in measuring the initial changes which take place. It is said to give a quantitative measure of these changes before the stage of positive Kreis tests has been reached. The taste of rancid butter fat produced by irradiation of ether and petroleum ether solutions in the presence and absence of air may be the resultant of two different changes, one due to structural changes in the glycerol portion and the other in the constituent to which the fat owes its original taste. These changes may occur independently.⁶² The distinction between rancid and tallow-like odors and tastes has been denied by Horowitz-Vlasova, Kachanova and Tkachev,⁶³ since both seem associated with the formation of various oxidation products such as hydroxystearic acid and epihydrinaldehyde. Lipolysis does not occur. Exposure of milk to sunlight catalyzes the oxidation of the fat.⁶⁴ Light also increases the peroxide number of butterfat.⁶⁵

Effects of Colors of Protective Wrappers. Discrepancies are apparent in the reports on the effects of various colors on the deterioration of oils. Greenbank and Holm,⁶⁶ Lea⁶⁷ and Coe⁶⁸ found green light to be least and orange light the most active. Blue light was thought to be somewhat more active than red light. Coe believed that oils protected by opaque or green wrappers showed no organoleptic rancidity after seven months, although they gave strong Kreis,

⁵⁹ Coe, M. R., *Oil and Soap*, **15**, 230 (1938); *Chem. Abs.*, **32**, 8178 (1932).

⁶⁰ Coe, M. R., and Leclerc, J. A., *Ind. Eng. Chem.*, **26**, 245 (1934)

⁶¹ Lampitt, L. H., and Sylvester, N. D., *Chim. et industrie, Special No. 642* (March, 1931); *Chem. Abs.*, **25**, 3737 (1931).

⁶² For a general discussion of the chemistry of rancidity, see Russell, E. E., *Can. Chem. Met.*, **20**, 346 (1931).

⁶³ Horowitz-Vlasova, L. M., Kachanova, E. E., and Tkachev, A. D., *Z. Untersuch. Lebensm.*, **69**, 409; *Chem. Abs.*, **29**, 7679 (1935).

⁶⁴ Barkworth, H., *Dairy Inds.*, **3**, 7 (1938); *Chem. Abs.*, **32**, 2230 (1938).

⁶⁵ Ritter, W., and Nussbaumer, T., *Schweiz. Milchztg.*, **64**, 59 (1938); *Chem. Abs.*, **32**, 7148 (1938).

⁶⁶ Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem.*, **25**, 167 (1933).

⁶⁷ Lea, C. H., *J. Soc. Chem. Ind.*, **52**, 146T (1933).

⁶⁸ Coe, M. R., *Siebel Tech. Rev.*, **9**, No. 2, 51 (1934); *Science*, **75**, 585 (1932); *Ind. Eng. Chem.*, **26**, 245 (1935); Coe, M. R., and Leclerc, J. A., *Cereal Chem.*, **9**, 519 (1932); *Chem. Abs.*, **26**, 6030 (1932); *Cereal Chem.*, **11**, 241 (1934); *Chem. Abs.*, **28**, 4925 (1934); *Oil and Soap*, **11**, 189 (1934); *Brst. Chem. Abs.*, **B**, 1018 (1934); *Oil and Soap*, **12**, 231 (1935); *Chem. Abs.*, **29**, 8371 (1935); *Oil and Soap*, **13**, 197 (1936); *Chem. Abs.*, **30**, 6587; *Oil and Soap*, **14**, 171 (1937); *Chem. Abs.*, **31**, 6494 (1937).

peroxide and von Fellenberg tests. Davies, however, believed⁶⁹ that the preservative effect of Cellophane wrappers depends more upon the depth of color than upon the actual color. Deep green, blue, red or dark brown were equally effective in preventing the autoxidation of the fat of biscuit meal in exposures of forty hours to sunlight. Light green and heliotrope wrappers allowed some oxidation to occur and lightly tinted papers were entirely ineffective. Thin vegetable parchment did not allow active rays to pass, greaseproof paper allowed some to penetrate and transparent paper had no retarding action.

Morgan⁷⁰ attacked the conclusions of Greenbank and Holm and of Coe. He finds in studies on potato chips that yellow or red light has little ability to cause rancidity, the deleterious action being due chiefly to blue and ultraviolet light. He did not rely, as others had done, upon oxygen uptake or the peroxide test, but determined the time of exposure required for rancidity to become evident to odor and taste. The ratio of this to the time required for the same effects to be

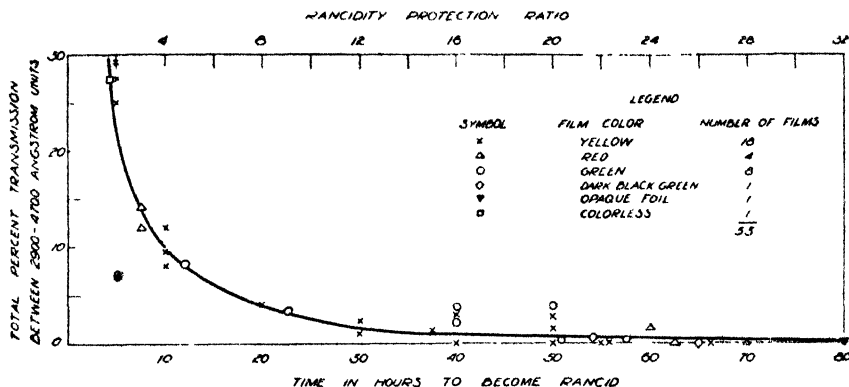


FIGURE 120. Rate of Rancidity Development in Potato Chips as Affected by Total Percentage Transmission of Light Wave-lengths 2900 to 4700Å (Morgan, *Industrial and Engineering Chemistry*).

produced in the same lot of chips simultaneously exposed in uncolored transparent cellulose gave the rancidity-retarding value of the film. Both daylight and a General Electric S-2 sunlamp were used as sources. It was believed that the rancid odor and taste are due to aldehydes of high molecular weight formed by the oxidation of unsaturated linkages. Tests of several hundred colored transparent cellulose wrappers indicated that their utility in retarding rancidity depended upon their transmission of blue and ultraviolet light. (See Figure 120.) Very small amounts of ultraviolet light had an extremely disproportionate effect. The results of the earlier observers were ascribed to their failure to take into account the passage of small amounts of ultraviolet light through some of their wrappers. The visible color tells nothing regarding the effectiveness of a wrapper. Morgan developed a yellow transparent sheeting of cellulose, known as Sylphrap RR Old Gold⁷¹ (from Sylvania Corporation) of high visible transparency and complete ultraviolet opaqueness in the usual 0.001-inch thickness. The only visible light cut

⁶⁹ Davies, W. L., *J. Soc. Chem. Ind.*, **53**, 148T (1934).

⁷⁰ Morgan, W. L., *Ind. Eng. Chem.*, **27**, 1287 (1935).

⁷¹ Morgan, W. L., *Modern Packaging*, May, 41, November, 34 (1934).

off is blue and practically all articles and foodstuffs wrapped in it appear in approximately normal color shades of red, brown, yellow or green. It is also recommended for protecting flavors of fruit juices, wines, brandies, flavoring extracts and perfumes as well as such drugs as phenol, calomel, quinine sulfate, and chloramine-T. It also retards the yellowing of paper and the sunlight aging of rubber.⁷²

Wickmann⁷³ employs a deposit of particles of metal of atomic dimensions on the surface of gelatin or cellulose sheets in a granular non-flaking and non-cracking layer, giving the appearance of a continuous, lustrous coating.

As absorbing agents, Hunter proposes,⁷⁴ for incorporation in cellulosic wrapping paper, diaminobenzophenone and its homologs, derivatives of phenylhydrazine and aliphatic keto-acids, aminonaphthalenesulfonic or trisulfonic acids, *p*-hydroxyazobenzene, diphenylaminobenzene, resorcinolazobenzene or cresolbenzene. These absorb over the range 3200 to 4000Å, and particularly 3500 to 3700Å. Grant⁷⁵ employs on regenerated cellulose wrappers a coating composition of pyroxylin 3, amyl acetate or other solvent 5-25, a colorless absorber of ultraviolet light, such as esculin, 0.5-5.0, monoethyl ether of ethylene glycol for blending 3-10, a low-boiling solvent, ethyl acetate or acetone, 11-30, castor oil or other plasticizer, 2-5 parts, and a diluent such as benzene, toluene or naphtha.

In Germany, there is used for the protection of butter a parchment paper known as "Ultrament." This excludes practically all rays between 3540 and 2000Å. Schlemmer⁷⁶ found one sample to show slight transmission at 2640Å. It prevents tallowiness when used at 5°C.⁷⁷ but it cannot prevent that tallowiness which arises from the catalytic action of iron which may have been present in the wash water, a process in which light is not concerned. It does not affect bacterial growth on butter, so that rancidity may still develop from this cause.

Commercial parchment is opaque in the entire ultraviolet and infrared regions, according to Solechnik.⁷⁸ The transparency increases, however, after prolonged exposures to the weather, because of natural bleaching processes.

Parchment paper may be treated with various pyrene compounds such as sodium 3,5,8,10-pyrene tetrasulfonate, sodium 3-benzoyl-aminopyrene-*p*-disulfonate and the urea of sodium 4'-aminobenzoyl-3-aminopyrene disulfonate.⁷⁹ In other filters, one part of 3,5-dimethoxypyrene is dissolved in 99 parts of nitrocellulose lacquer and the solvent evaporated to leave a colorless film insoluble in water. A film of cellulose hydrate may also be passed through a bath containing 1 per cent

⁷² Morgan, W. L., U. S. P. 2,043,860, June 9, 1936; *Chem. Abs.*, **30**, 5442 (1936); British P. 453,438, Sept. 8, 1936; *Chem. Abs.*, **31**, 1113 (1937). Dyes are used incorporated in regenerated cellulose sheets. Joseph, C., U. S. P. 2,038,114, April 21, 1936; *Chem. Abs.*, **30**, 3913 (1936); British P. 410,170, May 10, 1934, *Chem. Abs.*, **28**, 6312 (1934) uses as the absorbing agent a nonglucosidic coumarin derivative such as umbelliferone-acetic acid. Esculin, quinine, salol and anthracenes are also suggested. All patents to Sylvania Industrial Corp.

⁷³ Wickmann, P. A., U. S. P. 2,039,372, May 5, 1936, to Sylvania Industrial Corp.; *Chem. Abs.*, **30**, 4232 (1936).

⁷⁴ Hunter, A. S., French P. 791,492, Dec. 11, 1935, to Soc. des usines chimiques Rhône-Poulenc; *Chem. Abs.*, **30**, 4232 (1936); Hunter, A. S., U. S. P. 2,062,179, Nov. 24, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **31**, 789 (1937); Hunter, A. S., U. S. P. 2,129,131-2, Sept. 6, 1938, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **32**, 8618 (1938).

⁷⁵ Grant, D. H., U. S. P. 2,058,786, to Stanco, Inc.; *Chem. Abs.*, **31**, 187 (1937).

⁷⁶ Schlemmer, F., *D. Molkerei-Ztg.*, **56**, 185 (1935); *Chem. Abs.*, **29**, 2611 (1935); for a detailed discussion of factors affecting the deterioration of butter, see Jensen, J., and Ritter, W., *Lait*, **18**, 758 (1938); *Chem. Abs.*, **32**, 7147 (1938).

⁷⁷ Maier, Fr., *D. Molkerei-Ztg.*, **55**, 1477 (1934); *Chem. Abs.*, **29**, 2611 (1935).

⁷⁸ Solechnik, N. Y., *Bumazhnaya Prom.*, **13**, No. 8, 24 (1934); *Chem. Abs.*, **29**, 1244 (1935). See also Sommer, H., and Becker, J., *Zellstoff u. Papier*, **13**, 335 (1933); *Chem. Abs.*, **27**, 4669 (1933).

⁷⁹ British P. 457,708, Nov. 30, 1936, to J. G. Farbenind. A.-G.; French P. 804,582, Oct. 27, 1936; *Chem. Abs.*, **31**, 3602 (1937); see also Eggert, J., and Wendt, B., German P. 640,908, Jan. 15, 1937, who use a urea derivative of sodium *p*-aminobenzoyl-*p*-phenylenediamine sulfate; *Chem. Abs.*, **31**, 5484 (1937).

of the urea of sodium 4'-aminobenzoyl-3-aminopyrene-disulfonate at 50°C. so that every part of the foil is covered by the liquid for one minute.

Gerngross and Callo⁸⁰ use a dilute aqueous solution of pine-bark or quebracho extract in treating transparent papers or films of cellulose derivatives to make them impermeable to ultraviolet rays.

Paper milk bottles protect skim milk, whole milk or buttermilk against the action of sunlight in causing burnt flavors, but they do not protect whole milk or cream or homogenized whole milk and cream against tallowy flavors.⁸¹ The burnt flavor predominates in low-fat and the tallowy flavor in high-fat products. Both commonly occur together in whole milk exposed to the sun. Homogenization of milk and cream accelerates the development of tallow flavor in sunlight, but retards that due to copper catalysis. The burnt flavor may have its source in the protein-free serum. It seems to be related to the fading of lactoflavin, which is the primary cause of the bleaching of milk in sunlight. This bleaching does not occur in paper bottles.

Ried⁸² believed the stability of milk could be improved by keeping it in metal cans which had been previously irradiated by ultraviolet rays. He also proposed to pack butter and cheese in irradiated metal foil and believed the growth of yeast could be influenced by the use of irradiated metal vessels.

Soap bars with traces of iron or copper oxide darken in four days in diffused daylight and in a few hours in sunlight or ultraviolet light.⁸³ Sudden irregular after-darkening and rancidity of soap bars is traced to small quantities of rust or copper oxide from corroded parts of the equipment.

It has been claimed that a bactericidal substance may be obtained by irradiating a non-saponifiable portion of fatty material until it has an activity such that from 2 to 7 mg. per cc. of maize oil is fatal to yeast. Such a product may be mixed with inert oils or with lanolin to form medicinal preparations or may be added to cosmetics or shaving soaps.⁸⁴

⁸⁰ Gerngross, O., and Callo, A., British P. 459,335, Jan. 6, 1937; *Chem. Abs.*, **31**, 4021 (1937).

⁸¹ Doan, F. J., and Myers, C. H., *Milk Dealer*, **26**, No. 1, 76 (1936); *Chem. Abs.*, **31**, 2304 (1937).

⁸² Ried, O., Austrian P. 121,243, Sept. 15, 1930; *Chem. Abs.*, **25**, 2367 (1931).

⁸³ Wittka, F., *Seifensieder-Ztg.*, **54**, 740 (1927); *Chem. Abs.*, **22**, 177 (1928).

⁸⁴ British P. 423,354, Jan. 22, 1935, to Standard Brands; *Chem. Abs.*, **29**, 4526 (1935).

Chapter 30

Processes Involving the Polymerization of Oils, Paints and Varnishes

In discussing the bleaching of oils, it was impossible to avoid mention of the polymerization of unsaturated oils. The commercial processes which depend largely upon polymerizing and oxidizing effects are complex and are not as yet thoroughly understood. In addition, in unsaturated oils there are stereoisomeric transformations at double bonds. A separate treatment of these, and possibly other photochemical changes is scarcely possible as yet in a discussion of the mechanism of the drying of oils as influenced by light. Color changes also occur during drying.

Tung oil is the most suitable oil for studying the drying process because of its comparative freedom from mixed glycerides and because of its ability to yield purifiable products.¹ It was pointed out by Marcusson² that the white mass of melting point 32°C. formed in chinawood oil by ultraviolet light in the absence of oxygen cannot be a simple product of polymerization since the fatty acids liberated from it differ from those liberated from the original oil in melting at 71°C. They consist chiefly of β -eleostearic acid, an isomer of the α -form present in the original oil. Tung oil has 90 per cent of α -eleostearic (eleomargaric) acid. Accordingly, the formation of β -eleostearic acid is similar to the type of change discussed previously in connection with cinnamic acid. The formation of β -eleostearin causes the film of dried tung oil to lack durability. In addition to this process, there occurs also the formation of a small amount of an infusible polymerization product of β -eleostearin. This also is analogous to the type of change occurring in the cinnamic acid series. The change may be completed by 48 hours of irradiation, according to Böeseken and Ravenswaay.³

Manecke and Volbert noted⁴ that eleostearic acid and its methyl ester have a deep absorption band at 2650 to 2750 Å. Dingwall and Thomson⁵ went further in showing that two forms can be definitely identified by absorption curves. By studying the absorption spectrum of the α -form in alcoholic solution after various periods of mercury arc irradiation, it was found that during the first two minutes it tended to pass over into the β -form. Continued irradiation, however, caused profound changes. When a 15-per cent solution of the α -acid in 90-per cent alcohol was irradiated for two hours it was converted into an acid that had the same absorption spectrum (2500 to 2850 Å) as the acid obtained from the solid glyceride. The absorption curves obtained by Manecke

¹ A critical review of the earlier work on the drying of oils and the nature of the "oxyn acids" was given by Eibner, A., and Munzert, H., *Chem. Umschau*, **34**, 89, 101 (1927); *Brit. Chem. Abs.*, 417 (1927); *Chem. Abs.*, **21**, 2071 (1927). See also Morrell, R. S., *Chemistry and Industry*, **56**, 795 (1937).

² Marcusson, J., *Z. angew. Chem.*, **35**, 543 (1922); *Z. deut. Oel-Fett Ind.*, **43**, 162 (1923).

³ Böeseken, J., and Ravenswaay, H. J., *Rec. trav. chim.*, **44**, 241 (1925). Eibner, A., Merz, O., and Munzert, H., *Chem. Umschau*, **31**, 69 (1924); Nonaka, M., *J. Chem. Ind. Japan*, **24**, 1272 (1921); Morrell, R. S., *J. Chem. Soc.*, **101**, 2082 (1912). Blom, A. V., attributes the change to rays of long wave-length, *Chem. Umschau, Fette Oele Wachse Harze*, **36**, 229 (1929); *Chem. Abs.*, **23**, 6336 (1929).

⁴ Manecke, W., and Volbert, F., *Farben-Ztg.*, **32**, 2829, 2887 (1927); *Brit. Chem. Abs.*, **B**, 821 (1927).

⁵ Dingwall, A., and Thomson, J. C., *J. Am. Chem. Soc.*, **56**, 899 (1934).

and Volbert for linoleic acid and its ester were different. They resembled those of oleic and crotonic acids with a slight increase in the intensity of absorption and a displacement of the characteristic weak absorption bands in the direction of longer wave-lengths. Absorption curves for acetic, elaidic, linoleic, eleostearic and stearoleic acids have recently been given by van der Hulst.⁶ It will be recalled that in discussing the absorption of various unsaturated open-chain compounds, Smakula had shown the absorption to increase with the number of conjugated double bonds.

Eleostearic acid in carbon tetrachloride adds bromine rapidly in the light of a Uviol lamp until three double bonds are saturated.⁷

Eighteen grams of α -eleostearic acid in 180 gms. of petroleum ether in a freezing mixture was exposed by Bauer and Rohrback⁸ in a quartz flask to ultraviolet light while adding bromine dropwise to the extent of six atoms per molecule. A white solid which separated after several hours, during which there was much evolution of hydrogen bromide, had the formula $C_{18}H_{30}O_2Br_6$. On debromination with zinc in alcohol, it gave β -eleostearic acid. An oily by-product of the hexabromide had a bromine content between that of penta- and hexa-bromide. When debrominated, it gave an oil with a bromine content between di- and tri-bromoeleostearic acid.⁹ Of the three (conjugated) double bonds usually only two add bromine unless the solution is exposed to ultraviolet rays.¹⁰

Ellis found that chinawood oil at six inches from a mercury arc became so brittle after an hour that it could easily be pulverized to a white powder of iodine value 93. Linseed oil gave a resilient translucent jelly of practically the same color as the original oil.

Working with thin films of tung oil on glass slides, Eibner and Rossmann¹¹ found that exposure to sunlight or for ten minutes to a mercury arc causes a rapid formation of the crystalline β -eleostearin. Although at room temperatures, this is soluble in the unchanged oil, precipitation occurred if the film was kept at 0°C. The crystals could be observed microscopically under polarized light. This transformation is regarded as the first step in drying. In the absence of light, this isomerization did not occur. Oxygen is essential to the change of pure β -eleostearic acid to the amorphous condition, "filming"; this autoxidation is favored by light and by increase of temperature. The observation that during the conversion of this material into a film from 7 to 10 per cent of oxygen is absorbed invalidated the older theory that drying or film formation was a pure polymerization process. Examination of the fatty acids recovered from the product also showed that considerable oxidation had occurred. Polymerization probably also occurs so that film formation is a mixed process, "autoxypolymerization." Thus, if a tung oil containing β -eleostearin be exposed in a thin film, oxygen is primarily absorbed by the dissolved β -glyceride in the surface layers; the autoxypolymerization products are at first colloiddally dispersed and then, by rapid transition to the gel condition, constitute a first disperse phase leading to film formation. Comparative experiments on the behavior of thin and thick films showed that the absorption of oxygen continues up to the drying point, and constitutes a principal reaction. Not all of the original α -eleostearin is transformed to the β -form before the autoxypolymerization occurs, for a tung oil kept in darkness for three to four weeks dried to a clear film. The greater part is directly autoxidized to a film.

⁶ van der Hulst, L. J. N., *Rec. trav. chim.*, **54**, 639 (1935).

⁷ Kaufmann, H. P., and Luten-Berg, K., *Ber.*, **62B**, 392 (1929). In methyl alcohol, two of the double bonds are saturated in darkness within an hour but the third only begins to react after fifteen hours. *Ber.*, **59B**, 1390 (1926).

⁸ Bauer, K. H., and Rohrback, E., *Chem. Umschau Fette, Waxe, Harze*, **35**, 53 (1928); *Chem. Abs.*, **22**, 2073 (1928).

⁹ See also Kaufmann, H. P., *Ber.*, **59**, 1395 (1926); Böseken, J., *Rec. trav. chim.*, **46**, 619 (1927).

¹⁰ Kaufmann, H. P., and Baltes, J., *Ber.*, **69B**, 2670 (1936); *Chem. Abs.*, **31**, 2032 (1937).

¹¹ Eibner, A., and Rossmann, E., *Chem. Umschau*, **35**, 241 (1928); *Chem. Abs.*, **23**, 291 (1929); *Brit. Chem. Abs.*, **B**, 934 (1928). See also Merz, O., *Farbe und Lack*, **31**, 332, 343 (1926); *Chem. Abs.*, **21**, 184 (1927).

Microscopic examination of films of chinawood oil on glass revealed a shrinkage in volume and the formation of fine cracks while the film was still moist, the cracks reaching through to the bottom.¹² This contraction coincides with the formation of β -eleostearin from the α -form. The next step in drying is the formation of folds at right angles to the cracks, increasing the volume and frequently pushing the cracks together again to form a double-lipped joint; this folding coincides with the absorption of oxygen by the α -eleostearin. Certain observations, however, stand in opposition to this simple theory. β -Eleostearin alone, when melted, will show contraction and crack formation and, as previously stated, the β -form also dries by a primary oxidation followed by polymerization. Light seems essential to the wrinkling, since clear, non-wrinkled films are obtained by drying the oil in darkness. In the light of the quartz lamp, this oil never dries clear; in sunlight at lower temperatures, there is wrinkling without cracking. α -Eleostearin does not appear to cause cracking at room temperature. It has also been observed in a black wood oil varnish that a network of fine cracks can form after the wrinkles have appeared, passing through the latter at all angles. Rossmann¹³ states also that when ionized oxygen (produced by a flame, ultraviolet light or radioactive materials) was present during the drying of tung oil, wrinkles were formed, but that wrinkles did not form in the presence of ionized nitrogen or illuminating gas.

It has recently been suggested that a third form of eleostearic acid may exist. This is the punicic acid obtainable also from the seeds of the pomegranate. Ultraviolet light converts it into β -eleostearic acid.¹⁴

The properties of so-called "light-struck" tung oils were studied by Gardner and Parks.¹⁵ Upon heating, the oils were quickly transformed into a clear liquid condition and could then be used for the production of varnishes as satisfactory as those made from oils which had not been "light-struck." Oils which had been exposed to sunlight for about six months could be brought back to a normal state by heating to about 60°C., although then their solidification points were very much lower than those of normal oils. Warming samples of the exposed oils with an equal volume of acetone gave clear transparent solutions, but on standing overnight these solutions gave heavy deposits of white crystals. Eibner would doubtless consider these as β -eleostearin.

Rossmann¹⁶ exposed the α - and β -forms of eleostearic acid with and without solvents to sunlight and to the light of the quartz mercury arc. The products yellowed more or less, the iodine number decreased and the molecular weight increased. The decrease in iodine number determined by the usual methods did not indicate a loss of more than one double bond, but by the use of special methods it appeared to decrease by two in some cases. Various types of dimolecules may form through the loss of a double bond of each. It is also possible that the 1- and 6-carbon atoms of the three conjugated groups may join forming ring complexes. The amount of polymerization which occurs in 144 hours under the Hanau quartz lamp could be attained in a few minutes by heating at 300°C.

Lévy¹⁷ has also described the microscopic wrinkling and folding of the frosty surface of tung oil films dried in air and light. The films formed by the much slower drying of the oil in darkness (six to eight weeks) are, if thin, nearly or

¹² Eibner, A., and Rossmann, E., *Chem. Umschau*, **35**, 281 (1928); *Chem. Abs.*, **23**, 1516 (1929).

¹³ Rossmann, E., *Farben-Ztg.*, **38**, 1288 (1933); *Chem. Abs.*, **27**, 5557 (1933).

¹⁴ Farmer, E. H., and van den Heuvel, F. A., *J. Chem. Soc.*, 1809 (1936).

¹⁵ Gardner, H. A., and Parks, H. C., *Circular No. 256*, *Paint Manufacturers Association*, December, 1925.

¹⁶ Rossmann, E., *Fettchem. Umschau*, **40**, 96 (1933); *Chem. Abs.*, **27**, 5057 (1933).

¹⁷ Lévy, P., *Recherches et inventions*, **14**, 340 (1933); *Chem. Abs.*, **28**, 3918 (1934).

completely free from frostiness. When dried in light, but in the dry atmosphere of a sulfuric acid desiccator, three weeks are required and only the thin films exhibit frostiness. Drying in a dry or moist vacuum requires about a year, but the surface is smooth. There is a loss of 1 to 3 per cent in weight. On opening the tubes there is an ethereal odor. Pressed oils do not solidify even when exposed for several months to sunlight or to an electric filament lamp. Oil obtained by extraction with petroleum ether solidifies in from a few days to a year in darkness, in a few days to a month in sunlight and in a few hours in the light of a mercury arc lamp. X-ray diffraction diagrams indicate that the solidified oil has a crystalline structure. In studies by means of the Siedentopf cardioid ultra-microscope, McCloskey and France¹⁸ demonstrated a considerable increase in the number of colloidal particles and in the viscosity of tung and non-acidified linseed oils on irradiation.

Linseed Oil. The drying of linseed oil has been the subject of many investigations but cannot be said to be as well understood as is that of tung oil.¹⁹ Kaufmann²⁰ gave data on the effects of light on the rate of the bromination of linseed oil in carbon tetrachloride and in methyl alcohol saturated with sodium bromide. The results, in Table 23 cited by Knauss and Smull,²¹ are given as the equivalent of iodine absorbed by equal amounts of oil.

Table 23.—Bromination of Linseed Oil (Iodine No. 182)

Time	C Cl ₄		CH ₃ OH and NaBr	
	Dark	Sunlight	Dark	Sunlight
2 minutes	152.0	178.1
10 "	151.2	183.0	156.2	161.3
30 "	152.8	190.5	157.4	163.8
60 "	156.8	194.3	160.7	164.3
24 hours	183.0	239.5*	183.3	182.0
48 "	182.0	252.0	183.5	181.6

* No mention is made by Kaufmann as to whether any substitution had taken place to give these high values.

Knauss and Smull determined the rates of substitution and addition when bromine was kept with the fatty acids from poppyseed oil, soybean oil, linseed oil and perilla oil for one hour in darkness. They then observed increases in these values during subsequent exposure in quartz tubes to ultraviolet light during an hour. Similar observations were made upon oleic, linoleic and linolenic acids. The mixed fatty acids of the different oils all absorbed more bromine when irradiated than in darkness. This was held to indicate the presence of stereoisomers formed by light and not determinable by the usual methods of analysis. The possibility of a direct action of light upon the bromine does not seem to have been considered, probably because this effect would have been expected by visible rather than ultraviolet light.

Goldschmidt and Freudenberg²² found that ultraviolet light failed to cause the polymerization of linolenic acid and its esters *in vacuo*, the process occurring only through oxygen bonds. Genthe²³ made early studies of the use of ultraviolet rays in the drying of linseed oil. It was exposed on filter paper to an atmosphere of oxygen in a quartz flask. During the first two hours of irradiation the absorption

¹⁸ McCloskey, K. E., and France, W. G., *Ind. Eng. Chem.*, **27**, 160 (1935).

¹⁹ For a review of early work, see *Farbe und Lack*, 629 (1926).

²⁰ Kaufmann, H. P., *Z. Untersuch. Lebensm.*, **51**, 3 (1926); *Ber.*, **59**, 1390 (1926).

²¹ Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.*, **49**, 2808 (1927).

²² Goldschmidt, S., and Freudenberg, K., *Ber.*, **67B**, 1589 (1934).

²³ Genthe, A., *Z. angew. Chem.*, 2090 (1906).

of oxygen was slight. In the third hour, it became very rapid, gradually diminishing in rate during subsequent hours. No formation of ozone was noted.

In the laboratory of the senior author, samples of linseed oil were found to be considerably bleached by ultraviolet light²⁴ and in the case of the raw oil, practically no skin was formed over the top. With boiled oil, a film was formed in six hours if there was free access of air. In one case in which the oil was exposed in a thin layer over water, the oil became turbid and apparently a very stable emulsion was formed. In another case a sample of raw oil was exposed

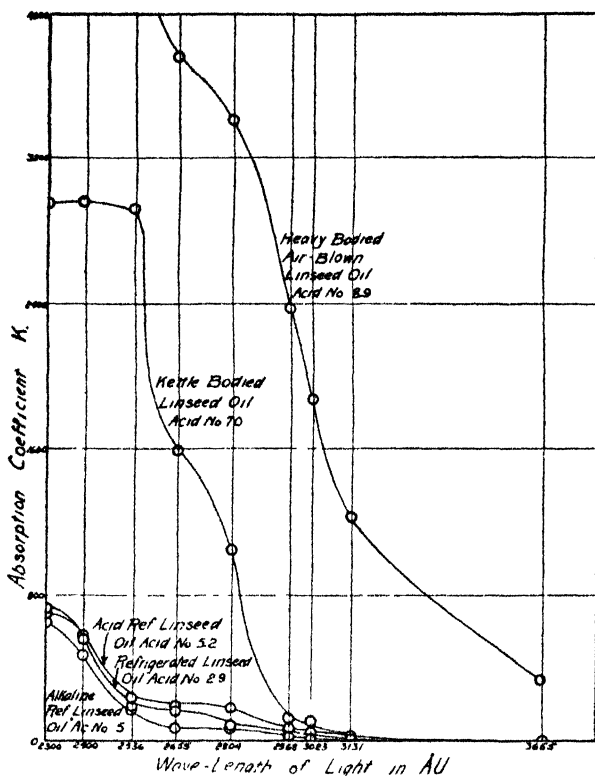


FIGURE 121. Absorption Shown by Several Samples of Commercial Linseed Oils (Stutz, *Industrial and Engineering Chemistry*).

for seven hours in a closed chamber in an atmosphere of steam. The oil, which had been quite dark at the beginning, was bleached to a light straw color.²⁵

Stutz²⁶ found the irradiation of raw linseed oil by ultraviolet in the presence of nitrogen to cause a marked decrease in the iodine number. This was confirmed by Knauss and Smull, who found that a sample of raw oil with iodine number of 180 showed only 148 after exposure for eighteen hours in dry carbon dioxide. But when this sample of oil was brominated in ultraviolet light for thirty minutes, the total bromine absorbed was equivalent to an iodine number of 190. In the

²⁴ See also Würth, K., *Farben Ztg.*, **33**, 1852 (1928); *Chem. Abs.*, **22**, 4261 (1928).

²⁵ Ellis, C., and Wells, A. A., *Chem. Eng.*, 116 (1918).

²⁶ Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1238 (1926).

first exposure of the raw oil in the presence of carbon dioxide, the ultraviolet rays caused a mutation of the stable isomers to labile forms. In the second exposure in which bromine was used, the action of the radiation stimulated the addition of halogen to the isomers formed in the first irradiation. It is known that labile isomers react very slowly with halogen and easily with oxygen. This too was found to be the case, for the oil from the first exposure (iodine number only 148) dried more rapidly than the raw, unexposed oil. It is apparent, therefore, that the

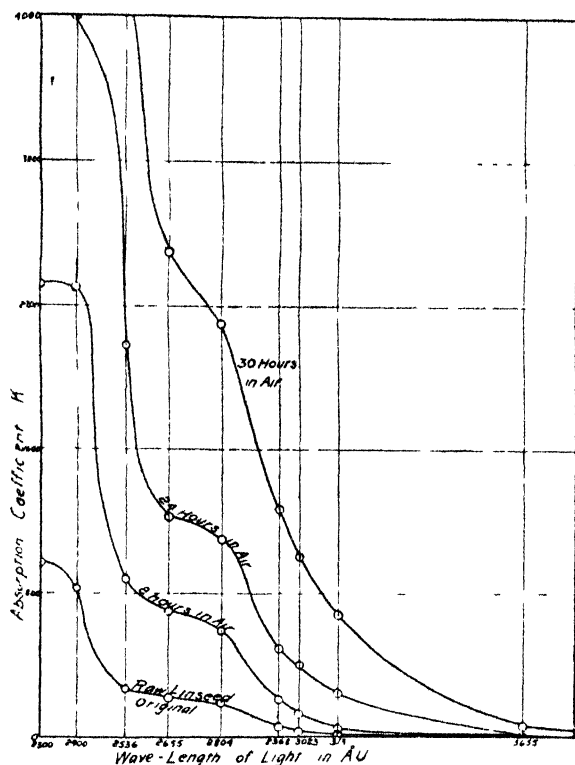


FIGURE 122. Change in Absorption Spectrum Shown by Raw Linseed Oil after Exposure to Ultraviolet Light in the Presence of Air (Stutz, *Industrial and Engineering Chemistry*).

ultraviolet rays must have simply stimulated the halogenation. It is unlikely that they could in thirty minutes have changed the labile form to the stable form.

An apparatus for oxidizing oils is described by Schofield.²⁷ The oil, such as linseed oil, is sprayed through a chamber illuminated by a high-tension electrical discharge. Purified and dried air is also supplied to the chamber, under pressure and at a temperature of about 250°C.

Gardner and Parks²⁸ found direct sunlight to accelerate the drying of a film of raw, unsiccated linseed oil exposed to the air. There were no differences in the drying times in direct sunlight or in sunlight filtered through plain, ground,

²⁷ Schofield, H., British P. 227,212, Oct. 16, 1923; *J. Soc. Chem. Ind.*, 180 (1925).

²⁸ Gardner, H. A., and Parks, H. C., *Circular 172*, U. S. Paint Manuf. Assoc., March, 1923.

red, amber, blue or green glass. When, however, diffused daylight was employed the following times of drying were noted: Pure unfiltered light, 4 days; amber glass, 11 days; blue glass, 13 days; darkness, plain glass, ground glass, red glass or green glass, 14 days. The effect of heavily siccating the oil was to cause the films under all conditions, including exposure in darkness, to dry in six hours. Previous exposure of a film of raw unsiccated linseed oil to the ultraviolet rays of an iron arc for thirty minutes produced a great acceleration in drying, which was shown to be independent of the heat resulting from the irradiation. When the ultraviolet rays were screened through red glass, the accelerating effect was lost.

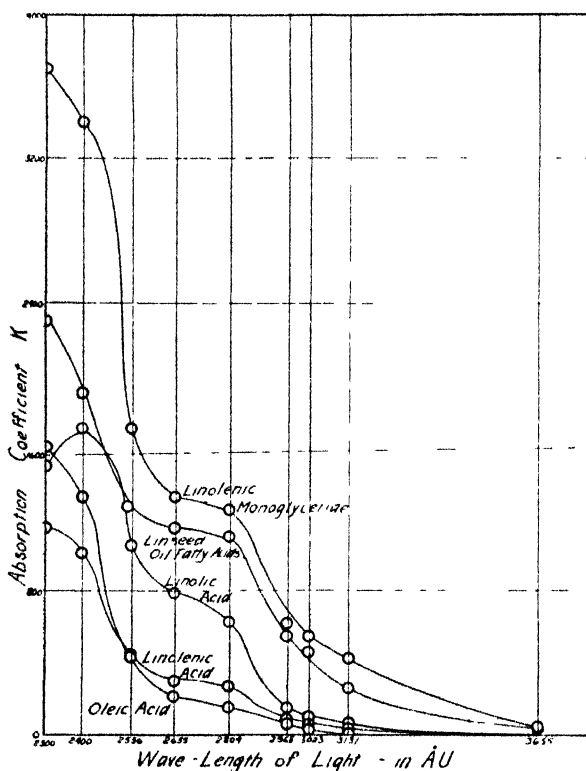


FIGURE 123. Absorption Shown by Acids Contained in Linseed Oil and Monoglyceride of Linolenic Acid (Stutz, *Industrial and Engineering Chemistry*).

Stutz²⁹ studied the influence of ultraviolet rays on a number of paint oils at 50°C., comparing their physical properties at various intervals. He also measured the absorption of the rays by these oils. In general, it increases with the molecular weight and body. The effect of exposure on wet oils is similar to the effect of heat and air-blowing. A boiled linseed oil absorbs the light almost completely at the surface. A raw oil, however, allows the light to penetrate a considerable distance. (Fig. 121 gives the absorption of several commercial samples.) Oils dried by exposure to ultraviolet light usually have a lesser absorption than those

²⁹ Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1235 (1926); **19**, 897 (1927).

dried in diffused daylight. (See Fig. 122.) Practically all the oils studied, including linseed, tung, soybean, poppyseed and perilla oils, have high absorption of wave-lengths shorter than those at the limit of the sun's spectrum. Because the absorption is so nearly complete near the surface, changes occur there only and the properties of the underlying film are less affected. The radiations of sunlight, however, can penetrate more deeply. This difference deserves consideration in interpreting the results of accelerated weathering tests discussed in a subsequent section. The longer the oil is exposed the more it absorbs and, therefore,

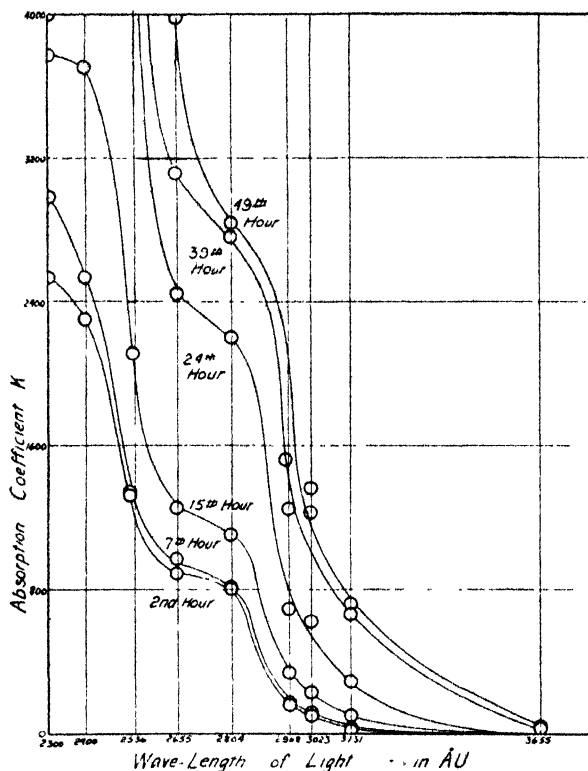


FIGURE 124. Absorption Shown by Several Samples of Linseed Oil Taken at Intervals during an Air-Blow (Commercial Scale) (Stutz, *Industrial and Engineering Chemistry*).

the greater the effect of light, which is cumulative. Bodding the oil seems merely to increase its content of absorbing materials. It cannot be due to an increase in acid content since the pure acids themselves have a lower absorption (see Fig. 123) than oil samples containing only 4 or 5 per cent of such acids. The similarity between the effects of ultraviolet on oil and the absorption changes during an air-blow of linseed oil (Fig. 124) make it probable that the decomposition or weathering of an oil film is simply a continuation of the drying of the film, the same reaction or reactions being involved in both.³⁰

³⁰ See also Becker, J., and Brückensteinkuhl, K., *Z. Kinderheilk.*, 43, 566 (1927). For some observations on the effects of light on sunflower oil, see Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhivoe Delo*, 12, 529 (1936); *Chem. Abs.*, 31, 5191 (1937).

Eibner and Munzert⁸¹ noted that a linseed oil film in direct sunlight can lose in weight (after a first sharp increase due to oxidation) and may resoften, so that the standard test should be made in diffused daylight. Two oils treated with ultraviolet light were found to have gelatinized throughout their bodies after standing in darkness for several months, their acetyl numbers rising from the original 1.5 and 2.8 to 60.7 and 71.39, respectively, and their hexabromide numbers dropping from the original 51.5 to 13.8 and 9.6, respectively. Their gasoline-insoluble hydroxyacids had increased from zero to 42.8. The normally dried films of linseed and poppyseed oils were thought to consist of glycerides of oxy-acids, although this could not be substantiated by chemical methods. The oxidized films are condensation products of the intermediately formed peroxides and are not true oxyglycerides.

Marling⁸² observed that linseed oil films without drier, or with a cobalt drier, on irradiation at 75 cm. from a mercury arc for a sixteen-hour period showed an increase in acid value and a decrease in iodine number. At a concentration of 0.015 per cent cobalt, the acid value reached 86 in this period. In an indoor aging test, 84 days were required for the oil to reach an acid value of 88.

It has recently been observed by Rose and Bolley that⁸³ unpigmented films of linseed oil, with or without drier, dry and harden when exposed under constant temperature and humidity to ultraviolet light, and then on continued exposure soften again. The percentage of the film insoluble in acetone reached a maximum at about the point of maximum hardness and decreased as the film softened again. The less saturated linseed oils gave dried films which softened less and were less soluble in acetone. Driers, lead or manganese, delayed and reduced the amount of after-softening. When pigmented with white lead, the films became progressively harder and less soluble with no after-softening. The iodine number, which was about the same for the soluble and insoluble portions of the film, decreased during exposure in all cases and was not related to the softening or solubility of the films.

Clark and Tschentke⁸⁴ made careful studies of the density changes during the drying of variously treated linseed oil films. For 32 hours of treatment by an intense sunlamp (equivalent to about six days of ordinary sunlight) the change in density varies from 2 to 4 per cent, depending on the drier. The highest change recorded was the unexpected one of 25.06 per cent for a raw oil film aged 226 days, though the density of this film had increased only 5.03 per cent in 68 days. This suggests that tests of linseed oil films must be run for a sufficiently long period. It also explains how paint films and patent leather may fail rather suddenly after a seemingly satisfactory period during several months. In the presence of driers this increase after periods of 248 days amounts to only 14 or 15 per cent.

Increases in density under ultraviolet light are smaller than in sunning, even though films may assume the same appearance and dryness. Where superposed films are involved, the mechanism of ultraviolet aging differs from that of sunning. After a film has been subjected to sunning or ultraviolet aging and is then placed in darkness, the increase in density continues at an increased rate. This is

⁸¹ Eibner, A., and Munzert, H., *Chem. Umschau Fette, Oele, Waxe und Harze*, **34**, 89, 101 (1927); *Chem. Abs.*, **21**, 2071 (1927).

⁸² Marling, P. E., *Ind. Eng. Chem.*, **21**, 594 (1929); see also Fukushima, I., Horio, M., and Miki, T., *J. Soc. Chem. Ind. Japan*, **35**, 142 (1932); *Chem. Abs.*, **26**, 3939 (1932).

⁸³ Rose, C. H., and Bolley, D. S., *Ind. Eng. Chem.*, **28**, 115 (1936).

⁸⁴ Clark, G. L., and Tschentke, H. L., *Ind. Eng. Chem.*, **21**, 621 (1929). A Mazda lamp source is used by Nicolson, D. G., and Holley, C. E., Jr., [*Ibid.*, **30**, 563 (1938)], who believe light destroys an inhibitor.

greatest after ultraviolet treatment. Although sunning requires hours, ultraviolet aging takes only minutes.

Auer⁸⁵ suggests treatment of linseed oil or castor oil with peroxides (*e.g.*, those of Mg, Zn, Ce or Na) and by heating at 250 to 300°C. under vacuum to obtain products which can be vulcanized and used as rubber substitutes. They may be employed also in the form of emulsions or as ingredients of varnishes, linoleum compositions, etc. In some cases, the products are further improved by exposure to ultraviolet rays or x-rays and by the use of such secondary reagents as formaldehyde, phenol, thiocarbanilide, benzidine, etc.

Experiments on the oxidation and polymerization of soybean oil were carried out by Taverne.⁸⁶ After ten days of exposure in air at room temperature, by Fahrion's method, the hydroxy-acids of three grams of oil on ten grams of cotton yarn were found to be 38.4 per cent. At 70° C., in the apparatus of Genthe⁸⁷ the oxidation was complete in thirty hours. By heating the irradiated oil in a beaker at 150° C., the molecular weight rose in ten days from 710 to 1730, indicating that polymerization accompanies oxidation. The oil became solid and contained 31.8 per cent hydroxy-acids and 63 per cent fatty acids soluble in petroleum ether, while the iodine number decreased to 64.8. Although Genthe had claimed that siccative oils can be bleached without oxidation, there was complete oxidation in 45 hours in Taverne's experiments. A lead (6.28 per cent) manganese (5.76 per cent) rosin compound was found to be the most active agent for hastening oxidation. On exposure to ultraviolet at 70°C., oxidation was complete with 5 per cent siccative oils in about ten hours.

Inaba, Kitagawa and Sato, and also Shinozaki and Sato,⁸⁸ exposed alcohol-extracted and benzene-extracted pressed soybean oils, both crude and refined, to ultraviolet light for sixty hours. After twenty hours, the alcohol-extracted and refined pressed oils were almost water-white, but it took thirty-five hours to decolorize crude pressed oil and benzene-extracted oil. Red colors were more easily bleached than yellow. The density, relative viscosity and refractive index increased with the time of exposure, sharply after fifty hours. For the first thirty hours the acid values remained constant, but after sixty hours they attained four to fifteen times their original values, reaching 4.5 to 5.5 no matter what they had been at the start. In the alcohol-extracted and refined pressed oils, the iodine numbers began to change after fifteen hours and in the benzene-extracted and crude pressed oils after thirty hours. After these periods, they decreased gradually. Fifty hours of exposure produced a substance soluble in petroleum ether; this amounted to 10 to 16 per cent after sixty hours. After 55 hours, the water-insoluble acids decreased by 2 to 5 per cent and the unsaponifiable matter increased 0.4 per cent. The oxygen content of the oils increased 4 to 5 per cent after ten hours. Both original and treated oils gave a weight increase of 6 to 7 per cent after 33 days. The ultraviolet absorption spectra also changed during the treatment, the oils becoming more opaque to the ultraviolet and less so to the visible rays.⁸⁹

The carbon arc greatly accelerates the drying of various oils. Perilla oil set

⁸⁵ Auer, L., U. S. P. 1,980,366, Nov. 13, 1935; *Chem. Abs.*, 29, 254 (1935), see also French P. 652,796, Oct. 4, 1926; *Chem. Abs.*, 23, 3804 (1929). British P. 321,690, 1929.

⁸⁶ Taverne, N., *Z. angew. Chem.*, 28, (I), 249 (1915).

⁸⁷ Genthe, A., German P. 223,419, Aug. 24, 1907; *J. Soc. Chem. Ind.*, 1168 (1910); *Chem. Abs.*, 4, 3146 (1910). In this, the oil or fat at 70-90°C. is treated with rays from an immersed mercury arc while air is blown through the hollow arm of a stirrer. It is claimed that 1000 kilos of linseed oil can be bleached with an expenditure of 60 k.w. hours for current, 30 h.p. hours and 1500 cubic meters of compressed air for stirring.

⁸⁸ Inaba, T., Kitagawa, K., and Sato, M., and Shinozaki, Y., and Sato, M., *J. Soc. Chem. Ind. Japan*, 37, 372, 374 (1934); *Chem. Abs.*, 28, 7046 (1934).

⁸⁹ For further studies of the influence of air, oxygen, hydrogen peroxide, diffused daylight, direct sunlight and ultraviolet light on the physical properties and oxidation of soybean oil, see Horovitz-Vlasova, L. M., Katschanova, E. E., and Tkatshev, A. D., *Z. unters. Lebensm.*, 69, 409 (1935).

to touch in two hours.⁴⁰ Oils such as candlenut, poppyseed, menhaden and soybean set to touch in four to seven hours. The so-called semi-drying oils, corn, cottonseed and rubberseed, were found to dry in about 24 hours. Gardner⁴¹ described apparatus suitable for drying newly painted walls.

In drying tests at the Institute of Paint and Varnish Research in Washington,⁴² there is employed a metal drum revolving in thirty minutes and surrounding a low-pressure quartz mercury arc. In this apparatus perilla and linseed oils containing 0.02 per cent of cobalt became solid in 24 hours and tung oil in four hours. These products yield to hot acetone 20, 32 and 16 per cent, respectively, of unpolymerized products. The polymerized, sponge-like residues, after drying, were tested to determine the amount of a petroleum distillate they could absorb. That from perilla absorbed 70 per cent, from linseed oil 80 per cent and from tung oil 160 per cent of the mineral spirits before the surfaces of the particles appeared wet. These preliminary results indicated the possibility of producing these solid products from oil economically. Tung oil treated with 0.05 per cent sulfur produced a wax-like mass resembling a hydrogenated fat, which might be used in linoleum manufacture.

The yellowing of oxidized drying oils cannot be due to the presence or formation of ketohydroxy- compounds in the film, according to Elm and Standen,⁴³ since ketohydroxystearic acid is colorless, although diketostearic acid is yellow. From their appearances in filtered ultraviolet, the yellowing differs in tung and linseed oil films.⁴⁴

Castor oil exposed to the sun in a thin layer solidifies fairly rapidly.⁴⁵ Polymerization of pilchard oil by ultraviolet rays shortens the induction period for its oxidation, and increases the rate of the process and the total amount of oxygen absorbed.⁴⁶

The densities, refractive indices and saponification numbers of sunflower-seed oil samples are gradually increased by ultraviolet irradiation. The acidity increases comparatively little, the iodine number drops toward the end of a series of thirty irradiations (2 to 6 hours) at ten-day intervals. The acetyl number at first rises and then drops. The oil is bleached considerably.⁴⁷

When fully extracted oil of the kernels of *Telfairia occidentalis*, which contains α -eleostearic acid, is exposed to diffused light for some weeks, very small yields of the β -isomer are formed. The yield is greatly increased by exposure to ultraviolet rays for some hours.⁴⁸

In the oil of the pits of the Brazilian oiticica tree, the chief constituent is licanic acid (4-oxo-9,10,11,12,13,14-octadecatriene-1-carboxylic acid), which resembles eleostearic acid in being extraordinarily sensitive to light and air. The three double bonds make possible the existence of eight isomers, of which two are known. The fresh oil contains α -licanic acid, as glyceride which when illuminated in the presence of a trace of iodine, gives β -licanic acid.⁴⁹

⁴⁰ U. S. Bureau of Standards Notes, *J. Frank. Inst.*, 206, 694 (1928).

⁴¹ Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ.*, 335, July (1928), 592; 330, 482 (1928); *Chem. Abs.*, 22, 3539 (1928).

⁴² *Ind. Eng. Chem.*, 22, 378 (1930).

⁴³ Elm, A. C., and Standen, G. W., *Ind. Eng. Chem.*, 24, 1044 (1932).

⁴⁴ Eibner, A., *Paint Varnish Production Mfr.*, 14, 7, 10, 14, 12, 30, March, 1936; *Chem. Abs.*, 30, 2779 (1936).

⁴⁵ Sunder, C., *Bull. soc. ind. Mulhouse*, 102, 353 (1936); *Chem. Abs.*, 30, 7348 (1936).

⁴⁶ Denstedt, O. F., and Brocklesby, H. N., *J. Biol. Board Can.*, 1, No. 6, 487 (1936); *Chem. Abs.*, 30, 2784 (1936).

⁴⁷ Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhirovoe Delo*, 12, 529 (1936); *Chem. Abs.*, 31, 5191 (1937).

⁴⁸ Farmer, E. H., and Paice, E. S., *J. Chem. Soc.*, 1630 (1935).

⁴⁹ Brown, W. B., and Farmer, E. H., *J. Chem. Soc.*, 1632 (1935).

Pigments. The effect of ultraviolet light on the darkening of lithopones has been discussed in Chapter 21. Some application has been made of ultraviolet-induced fluorescence methods in the determination⁵⁰ of the nature and quality of pigments, but many variable factors exist and careful control and considerable experience are necessary. The method is said to be valueless for estimating the pigment value of lithopones or zinc white, but natural and precipitated chalks may be distinguished by their appearances in ultraviolet light.⁵¹ The presence of 25 per cent of zinc oxide in titanium white changes the violet fluorescence of the latter to a greenish yellow. The admixture of organic coloring matters in mineral pigments can frequently be detected by this method.

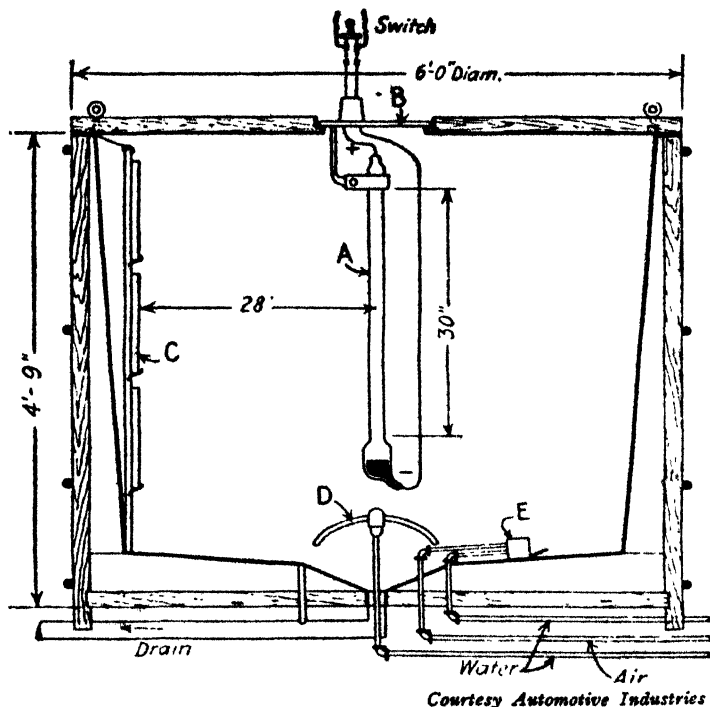


FIGURE 125. Nelson Exposure Tank.

Kurotaki and Kobayashi⁵² introduce 5 to 20 per cent of trivalent nitrogen organic compounds without acyl, alkyl or alkylene groups or their aldehyde condensation products in order to increase the light-fastness of pigments. Among the compounds used are α -naphthylamine, phenylenediamine, phenylazobenzene, phenylhydrazine and diazoaminobenzene.

The one salutary effect of light on paints is its bleaching action on yellowed surfaces. Whereas light of wave-length 3200A or less is required to produce pronounced deterioration of paints and darkening of lithopones, the beneficial bleach-

⁵⁰ Kufferath, A., *Farbe und Lack*, 473 (1935); Grant, J., *Oil and Colour Trades J.*, 85, 1601 (1934); *Chem. Abs.*, 28, 5997 (1934); *Paint Manuf.*, 7, 340 (1937); Elm's, J., *Rev. gén. mat. plastiques*, 14, 154 (1938); Bandel, G., *Anacw. Chem.*, 51, 570 (1938).

⁵¹ Schoen, M. J., and Ruise, J., *Chem. Weekblad*, 26, 321 (1929); *Brit. Chem. Abs.*, B, 609 (1929).

⁵² Kurotaki, S., and Kobayashi, C., Japanese P. 110,746, May 13, 1935; *Chem. Abs.*, 30, 2411 (1936).

ing action extends to much greater wave-lengths, in fact, up into the visible spectrum, according to some qualitative observations of Pfund.⁵³ On the other hand, in the case of nitrocellulose lacquers, the addition of any such plasticizers as dibutylphthalate, tricresyl phosphate, Sipalin AOM and Sipalin MOM increases the yellowing of the films on exposure to ultraviolet light, the effect being greatest with tricresyl phosphate, next with butylphthalate, next with Sipalin MOM and least with Sipalin AOM.⁵⁴



Courtesy National Carbon Co., Inc

FIGURE 126. Paint and Varnish Test Using Eveready C₆A Unit

Accelerated Weathering Tests.⁵⁵ Accelerated weathering tests for paint films have been devised by many, and usually involve the use of some ultraviolet light source to bring about in a short time the effects of sunlight over a prolonged period. It is readily apparent that there should be no reason to expect the short

⁵³ Pfund, A. H., *Proc. Am. Soc. Testing Materials*, 23, II, 377 (1923)

⁵⁴ Wolff, H., and Rosen, B., *Farben Ztg.*, 34, 2564 (1929); *Chem. Abs.*, 23, 4835 (1929)

⁵⁵ A brief account of the historical development of accelerated paint tests has been given by Würth, K., *Farben Ztg.*, 33, 1470 (1928). For a general discussion of radiation and paint, see New, G. F., *Paints Manuf.*, 6, 145-6; *Oil Colour Trades J.*, 89, 787 (1936), and Masseille, H., *Peintures, pigments, vernis*, 8, 1478 (1931).

wave-length, highly active radiations to produce effects similar to those of the longer wave-lengths present in sunlight. Nevertheless, when their limitations are borne in mind, the use of ultraviolet tests may furnish in a short time comparative data which may be useful although they may not be in complete agreement with the results of prolonged fading tests.

Nelson⁵⁶ used a wooden exposure tank surrounded by an insulated air-space and lined with galvanized iron and containing a cylinder which revolves the test panels in a 24-hour cycle. Effects of sunlight, rain and mist were simulated by a quartz mercury arc, a revolving spray and a water-atomizer, respectively, together with a variable-speed electric fan to cool the arc and maintain a uniform temperature. (See Figure 125.) A more recent testing tank employs a carbon arc. (Figure 126.)

A cycle of exposure for 24 hours to the rays of the arc at a temperature of 50 to 60°C., followed by cooling and exposure to the water spray for another 24 hours at 5 to 10°C. was chosen as representing actual service conditions. Exposures were made at a distance of 28 inches from the source of the rays, investigation proving that the useful rays of destructive effect had a wave-length in the neighborhood of 3000Å. On an average, comparable results were obtained in as many days in the apparatus as in months under service conditions. The following results were obtained on a series of paints, the figures referring to the number of days necessary for complete loss of gloss, and for initial chalking, respectively: 100 per cent lead-free zinc oxide, 14, 16; 100 per cent leaded (35 per cent) zinc oxide, 9, 12; 100 per cent light-resistant lithopone, 4, 6; 100 per cent basic lead carbonate, 3, 5; 100 per cent Titanox, 2, 4; a mixture of 40 per cent zinc oxide, 40 per cent lithopone, 20 per cent whiting, 9, 11. The effect of periodic saturation and maintenance of a saturated atmosphere during exposure is to accelerate both complete loss of gloss, and initial chalking by 50 per cent. Freezing of a saturated film materially promotes the formation of removable "chalk," most probably due to the formation of ice within the film. Neither flaking nor checking was reproduced in any of these tests. Cracking, rapidly followed by scaling and peeling, is produced by periodic exposures to temperatures considerably below freezing point, and is reproducible by exposures of equal alternate intervals to radiation, low temperature, and water-spray for a period of 100 days, equivalent to 14 to 15 months' exposure to the weather. Lack of adherence is a fault more strictly connected with the method of application of the paint, but can be brought about by exposure at 50 to 60°C. to the mercury arc. Of commercial paints intended for use as protective coatings for iron, both a 100 per cent red-lead paint and a mixture of 85 per cent ferric oxide with 15 per cent zinc oxide showed outstanding merit in maintaining gloss and inhibiting the formation of rust as compared with iron oxide paints containing various fillers, and a zinc oxide sublimed lead paint also containing a filler. Although a certain light-resistant lithopone maintained its whiteness over a period of three years on exterior exposure, the effect of the ultraviolet radiations was to discolor both this product and white lead in a short time.

Films exposed to ultraviolet rays increase in tensile strength and decrease in extensibility.⁵⁷ This effect is less pronounced with films containing zinc oxide, which is opaque to ultraviolet rays, than with films containing basic carbonate white lead, which is more transparent. The hardening and subsequent disintegration of the surface of a linseed-oil binder through reactions induced by ultraviolet radiation must be recognized as a fundamental cause for the failure of paints by chalking. This effect may be reproduced on pigments such as basic carbonate white lead by ultraviolet exposure alone without introducing any temperature or moisture variations.

Verification of the deteriorating effects of ultraviolet light came quickly from a number of sources. Thus, Wagner⁵⁸ claimed that the quartz mercury-vapor

⁵⁶ Nelson, H. A., *Proc. Am. Soc. Testing Materials* 22, II, 485 (1922).

⁵⁷ Nelson, H. A., and Rundle, G. W., *Proc. Am. Soc. Testing Materials*, 23, II, 356 (1923); *New Jersey Zinc Co. Research Bull.*, March, 1930.

⁵⁸ Wagner, H., *Farben Ztg.*, 30, 2991 (1925); *Chem. Abs.*, 19, 3602 (1925); *Farben Ztg.*, 31, 1023, 1073 (1926); *Z. Angew. Chem.*, 38, 1191 (1935).

lamp gives the same final bleaching of 14 mineral pigments and 75 coal tar dyes as sunlight in one-fifth to one-thirtieth of the time, but noted that the type and quality of the vehicle influenced the results. The refractive index of the binding medium should be as near as possible to that of the pigment. In testing organic pigments or dyes, the least favorable medium for determining fastness to light is an aqueous glue wash, and the most favorable an oil or concentrated dextrin medium. The conversion factor of ultraviolet lamp hours into sun hours differs widely for different pigments.

Discrepancies between the results of accelerated tests and outdoor exposures gradually became apparent. Gardner and Parks⁵⁹ believed that, regardless of whether the accelerated test wheel would determine how a coating will wear on exterior exposure, it is of great value in securing quick data in regard to the comparative aging of experimental coatings. Furthermore, as Dean pointed out,⁶⁰ the results of outdoor exposure tests are subject to factors difficult to control, such as climate, temperature range and the rate of its variation, rainfall, humidity, wind, abrasive dusts and various gaseous contaminants of the air. This accounts for the effort spent by many workers in developing the better controlled accelerated testing methods.

Nelson and Schmutz⁶¹ balanced the weathering factors used in their tests to approximate at least roughly the order and relative magnitude of these factors as they appear in average outdoor weathering conditions. The weathering of a paint, varnish or lacquer surface may be considered a process of (1) rendering the film indistensible or (2) bringing about internal strains due to shrinkage, or both, and then of (3) revealing these weaknesses by the breaking up of the surface. The first of these usually involves oxidation, condensation and chemical decomposition. The second is usually due to temperature changes, which, in an indistensible film can be compensated for only by cracking and peeling.⁶²

The apparatus of Nelson and Schmutz⁶³ consisted of a circular exposure tank four feet in diameter and sixteen inches in height with the destructive light source at the hub. A water spray, a silica gel dehydrator, and heating and cooling coils were included in an air-circulating system. Gas inlets and outlets for the introduction of oxygen and ozone when desired were provided. Refrigeration and water spray exposures were carried out in separate units, although it was also possible to use the water spray in the light exposure chamber. As a source, the flaming arc of the Atlas Electric Devices Co. Fade-Ometer was preferred to the quartz mercury arc since its spectrum more closely resembles that of the sun. It has approximately 34 per cent of its intensity below 4100Å but none below 3100Å. In comparative tests employing the mercury arc and the treated carbon arc in similar cycles, panels with three coats of a house paint lost 76 per cent in gloss and chalked badly with the mercury arc; they lost only 13 per cent in gloss and did not chalk with the carbon arc. The temperature should be 140°F. and certainly not higher than 160°F. Although light exposures accompanied by high humidity might be expected to show great destruction, most failures such as chalking and checking, were noted during light exposures at low humidity when given immediately after high humidity exposures. From stress-strain measure-

⁵⁹ Gardner, H. A., and Parks, H. C., *Paint Mfrs. Assoc., U. S. Circular* 232, 248 (1925); *Chem. Abs.*, 19, 2560 (1925).

⁶⁰ Dean, H., *Chemicals* (Oct. 25, 7, 1926).

⁶¹ Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, 18, 1222 (1926).

⁶² Erosion is rarely considered. See Nelson, H. A., and Werthan, S., *Ind. Eng. Chem.*, 18, 965 (1926).

⁶³ Nelson, H. A., and Schmutz, F. C., *Proc. Am. Soc. Testing Materials*, 26, II, 563 (1926); Nelson, H. A., Schmutz, F. C., and Gamble, D. L., *Ibid.*, 26, II, 1 (1926).

ments on paint films, adsorbed water generally increases distensibility. Therefore, severer deteriorations may actually be taking place during a light exposure with high humidity but will not be so quickly revealed because of the additional distensibility induced by the adsorbed water. In a subsequent light exposure with low relative humidity, the previous weakening of the films shows up because the surface in the dry condition has a lower distensibility. This influence of humidity varies with the water resistance of the surface tested. In general, the humidity of the light exposure chamber should be made to conform to the ratio of high to low humidity conditions of the weather simulated. Checking, which was formerly difficult to reproduce in characteristic form, is promoted by the addition of oxygen up to 30 or even 100 per cent. In routine testing, 30 per cent is adopted. The temperature of the water spray is also of importance.

One month in a suitable weathering cycle should approximate fourteen months of outdoor exposure, when a suitable addition of oxygen is made.

The Bureau of Standards employed⁶⁴ a flaming carbon arc. The regular test program is made up of exposure to ozonized air for three hours, rain for three hours, light for seventeen hours and inspection one hour. In addition, on three days each week, the panels are subjected to refrigeration at -23°C . for one hour, one-half hour being subtracted from the periods for exposure to ozone and rain. The order of exposures is varied on different days.

In a more recent description of the Bureau of Standards method, Hickson and Walker⁶⁵ state that the chamber for exposure to light and moisture consists of a rotating cylinder made of No. 16-gauge galvanized iron 76 cm. in diameter, 38 cm. high, open at both ends with the light-source suspended in the center. This size was selected to bring the light as near the panels as possible, at the same time avoiding too high temperatures. The cylinder has a capacity for sixty 7.5×15 cm. panels. These are placed in two tiers immediately opposite the light inside the cylinder, the panels thus being 38 cm. from the center of the light source. This gives a temperature of about 50 to 55°C . at the panels with the type of lamps used. Thirty slotted holders 7.5 cm. wide and about 35 cm. long for the panels are attached to the open surface of the open cylinder. A pan placed about 5 cm. below the bottom of the light cylinder contains water and serves to keep the temperature next to the panels down to about 52°C . as well as to humidify the air. To duplicate sunlight reasonably, an enclosed type carbon arc light operated at 220 volts d.c. and 13 amps. is employed. On each renewal of the carbons, the glass globe (opaque to wave-lengths less than 3200A) should be cleaned. To simulate a hot, humid climate, a fixed water spray is mounted in the tank in such a manner that it may function while the lights are operating. The light cylinders rotate slowly at three revolutions per hour. An ammonia coil about $27 \times 47 \times 40$ cm. in an insulated chamber that can be cooled to -25°C . is used to chill the panels quickly. On removal from the light chamber, the test panels are placed in racks and the rack and samples are placed in the refrigerator, left there for one hour and then removed.⁶⁶

In a method employed in Germany by Schulz⁶⁷ the paints are applied to iron plates and allowed to dry for at least three days, then matured for 24 hours at 80°C . The subsequent treatment consists of six repetitions of the following cycle: hanging in distilled water at 20°C ., exposure to ultraviolet light while moist and again when dried,

⁶⁴ *Tech. News Bull., Bureau of Standards*, Sept. 4, 1927; Walker, P. H., *International Congress Testing Materials*, II, 603, 1927; *Chem. Abs.*, 23, 997 (1929).

⁶⁵ Hickson, E. F., and Walker, P. H., *Ind. Eng. Chem.*, 20, 591 (1928).

⁶⁶ Note also Davidson, J. G., and Reid, E. W., *Ind. Eng. Chem.*, 20, 199 (1928).

⁶⁷ Schulz, M., *Farben Ztg.*, 31, 2879 (1926); *Brit. Chem. Abs.*, B, 924 (1926); *Farben Ztg.*, 32, 2128 (1927).

re-immersion in distilled water, enclosure in a damp atmosphere containing carbon dioxide, further exposure to ultraviolet light under damp conditions, and then at 50°C., enclosure in an atmosphere containing sulfur dioxide, exposure to damp air at 35 to 40°C., with interpolated periods at -5°C., and renewed action of ultraviolet rays. It was claimed that the results on zinc oxide-lithopone paints showed agreement with a two-year exposure to the atmosphere, in that the iron plates showed increasing rusting with the increase in proportion of lithopone to zinc oxide in the protecting paint.

In a rapid-testing apparatus described by Blom,⁶⁶ two parallel chains are mounted on tiers of cog-wheels two meters apart so as to carry between them fifty test sheets 10×20 cm. The chains travel at 20 cm. per minute and carry the sheets through three heating chambers and one freezing box. Sprays are fitted between the chambers, one of which can be filled with corrosive gases if desired. The strips are also submitted to both ultraviolet light and the light from a Sollux lamp. A typical time of treatment is only five days. Another German test machine described by Ritter⁶⁷ is claimed to give results in from 32 to 60 hours. An accelerated test has been patented by Digby, King and Kelvin, Bottomley and Baird, Ltd.,⁷⁰ and others have been described by Walter⁷¹ and by Vila.⁷²

Inconsistencies between the results obtained by the ultraviolet methods and outside exposures have led to renewed study of the effects of various light sources. Zeidler and Toldte⁷³ exposed eleven paints with various lead pigments on iron panels to radiations from the sun, an arc light, a mercury arc and a Nitra lamp, in some cases with a previous exposure to the action of hydrogen sulfide. The relative effects of the various sources on different paints were not uniform. In general, the mercury arc effected the greatest degree of fading of the discoloration produced by hydrogen sulfide.

Schmutz and Gamble⁷⁴ investigated the effects of six impregnated carbon arcs of known spectral energy distribution, the untreated carbon arc and the mercury arc on lithopones in nitrocellulose lacquers. Intensification of the infrared and visible ranges had but little influence on the results. One sample was unaffected by intensification between 3200 and 4200Å. Two others were equally affected, although rays between 3000 and 3200Å brought out a difference between them, and caused some effect on a third sample unaffected by the longer rays. With radiations below 3000Å, the darkening was the same in the sample not affected at the longer wave-lengths and in only one of the two which had been equally affected by the longer rays. All samples showed up poorly. It is evident that specific wave-lengths exert specific effects on various samples of the same type of pigment. When wave-lengths shorter than 2500Å are employed, the differences between samples become less marked.

The chief difficulty in the use of the carbon arc is due to the heat generated, elaborate cooling systems being required for its use in closed systems. Preliminary experiments indicated that the suitability of the mercury arc for this work could be increased by the employment of filters of Corning glasses.⁷⁵ Vitrified quartz burners were believed to have the advantage of not completely transmitting the far ultraviolet and of being more rugged than fused quartz.

⁶⁶ Blom, A. V., *Chem. Fabr.*, 102 (1928); *Chem. Abs.*, 22, 3789 (1928).

⁶⁷ Ritter, E., *Kali*, 23, 10, 26 (1929); *Chem. Abs.*, 23, 2048 (1929).

⁷⁰ Digby, W. P., King, F. A., and Kelvin, Bottomley and Baird, Ltd., British P. 429,792, June 6, 1935; *Chem. Abs.*, 29, 7100 (1935).

⁷¹ Walter, P., *Bull. soc. encour. ind. natl.*, 134, 213 (1935); *Chem. Abs.*, 29, 5287 (1935).

⁷² Vila, A., *Recherches et inventions*, 16, 26, 349 (1935); *Chem. Abs.*, 29, 6441 (1935).

⁷³ Zeidler, G., and Toldte, W., *Farben Ztg.*, 33, 1507, 2607 (1928); *Chem. Abs.*, 23, 3585 (1929); *Farben Ztg.*, 34, 1547 (1929); *Brit. Chem. Abs.*, B, 365 (1929).

⁷⁴ Schmutz, F. C., and Gamble, D. L., *Ind. Eng. Chem., Anal. Ed.*, 1, 83 (1929); see also Gardner, H. A., and Sward, G. G., *Am. Paints Varnish Mfrs. Assoc., Circular 358*, 64 1930; *Brit. Chem. Abs.*, B, 622 (1930); Nelson, H. A., *First Communications, New International Assoc. Testing Materials*, Zurich, 117 (1933).

⁷⁵ See also Becker, E., *Farben Ztg.*, 33, 2232 (1928); *Chem. Abs.*, 23, 1290 (1929).

Sward and Hart⁷⁶ compared the outdoor weathering of a number of coating materials with that produced by (1) a pair of 13-amp. enclosed carbon arcs, (2) a 50-amp. flaming carbon arc with Sunshine carbons, (3) a similar one with therapeutic C carbons and (4) a low-pressure mercury in quartz arc. Typical outdoor-type failures were obtained with the first and second sources, the latter being two to three times faster than the former. Failure by chalking predominated with the third and fourth even in materials which out-of-doors failed by checking. A combination of sources might be used to produce both checking and chalking. The operating costs are approximately 22, 21, 21 and 8.5-13 cents per hour for the four sources, exclusive of capital investment.

There has been much general discussion of the applicability of these accelerated methods. Grunder and Shepherd⁷⁷ believed them useful in comparing colors of the same basic type. The need for more refined methods for detecting failures has frequently been emphasized.⁷⁸

The accelerated tests have the advantage of rapidity, constancy of results and ready adaptability to simulate peculiar exposure conditions.⁷⁹ Nettmann,⁸⁰ who is somewhat more critical of their value, attempted a theoretical discussion of the aging of paints on the basis of accumulation of potential energy in the films being responsible for changes in their inner structure. Nauroy⁸¹ pointed out that no accelerated aging test could give the paint user an absolute or even a comparative measure of the value of a product submitted to him. Nevertheless, such tests can be of considerable value to the manufacturer for rapid control of the effects of variations in formulas. Williams⁸² exposed panels of various yellow and green paints to ultraviolet light for 150 hours at 16 inches from the light. Warm air at 34°C. was continuously circulated around the panels. Failure was a darkening, probably the result of a reaction between paint and vehicle. Very pronounced chalking resulted but no great difference was apparent between panels of the same group. Gardner made some studies⁸³ of the water-soluble material produced by the action of weathering and ultraviolet light on various paints.

Sieplein⁸⁴ plotted the duration, intensity and fluctuational characteristics of outdoor ultraviolet radiation effective in exposure tests from astronomical and meteorological data for Miami and for a point representative of the eastern industrial region of the northern United States. Gardner⁸⁵ notes that paint films prepared indoors and stored in confined spaces often develop a mottled appearance when later exposed out of doors to the action of the sun.

The literature of the behavior of white pigments toward ultraviolet light has

⁷⁶ Sward, G. G., and Hart, L. P., *Am. Paint Varnish Mfrs. Assoc. Circular* 375, 53 (1931); *Chem. Abs.*, 25, 1105 (1931).

⁷⁷ Grunder, A., and Shepherd, R. S., *Paints, Oils Chem. Rev.*, 6, No. 6, 8, 25 (1928); *Chem. Abs.*, 22, 3538 (1928).

⁷⁸ Kempf, R., *Farben Ztg.*, 33, 2359 (1928); *Brit. Chem. Abs.*, B, 578 (1928); Walker, P. H., and Hickson, E. F., *Ind. Eng. Chem.*, 20, 591 (1928). Toldt, W., advocated the use of the Pulfrich step-photometer and the Ostwald color system for reporting the effect of light on paints, *Farben Ztg.*, 39, 140 (1934).

⁷⁹ Eibner, A., *Farben Ztg.*, 34, 322 (1928); *Brit. Chem. Abs.*, B, 63 (1929).

⁸⁰ Nettmann, P., *Farben Ztg.*, 34, 2181 (1929); *Brit. Chem. Abs.*, B, 609 (1929); *Farbe und Lack*, 77, (1931); *Chem. Abs.*, 25, 2009 (1931).

⁸¹ Nauroy, A., *Chimie et industrie*, Special No. 683 (March, 1932); *Chem. Abs.*, 26, 3681 (1932).

⁸² Williams, J. J., *Am. Paint Varnish Mfrs. Assoc. Sci. Section, Circular* 341, 879 (1928); *Chem. Abs.*, 23, 5334 (1929).

⁸³ Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ.* 313, 368 (1927); "Physical and Chemical Examination of Paints, Varnishes and Lacquers," 4th ed., 183, 308, 1927.

⁸⁴ Sieplein, O. J., *Natl. Paint Varnish Lacquer Mfrs. Assoc., Circular* No. 447, 1, (1934); *Brit. Chem. Abs.*, B, 209 (1934).

⁸⁵ Gardner, H. A., *Natl. Paint Varnish Lacquer Mfrs. Assoc. Circular* No. 455, 66 (1934); *Chem. Abs.*, 28, 3251 (1934). He describes an outdoor water-wheel test rack. *Natl. Paint Varnish Lacquer Assoc., Sci. Section, Circular* 534, 177 (1937); *Chem. Abs.*, 32, 3639 (1938).

been reviewed by van Hoek.⁸⁶ Wagner⁸⁷ states that the inferiority of the chalk paints to those made from barium or calcium sulfates is not due to their impermeability to ultraviolet light, which is about equal to that of paints with barytes and other white bases, but appears to be due to the flocculated condition of the chalk particles in the prepared paint, to the fineness of the particles, to their soft texture, to the high oil content of the paint and to its great tendency to swell. The usual discoloration of titanium white paint is ascribed by Zhukova and Sovalova⁸⁸ to the instability of the titanium dioxide-linseed oil system because of poor wettability of the oxide by the oil. By using an oxide ignited at 800°C. instead of at 600°C., the discoloration in darkness is greatly retarded and that in ultraviolet light is practically eliminated. Soaps have a similar effect by forming pigment-enveloping aggregates which prompt the dispersion of the oxide in the medium.

It is difficult to increase the fastness of chromes without adversely affecting the desirable properties of greening power or tinctorial strength and brightness of shade.⁸⁹

To understand the susceptibility of various paint films to ultraviolet light, it is necessary to know something of the absorption of the harmful radiations by the pigments, since if they are so absorbed, there will be less energy to be absorbed by the oxidized oil film and less resulting deterioration of the film. At the same time, it is also desirable to know the relative abilities of various pigments, fillers and paint films themselves to reflect ultraviolet light. This is of some importance in the development of special paints for covering walls of rooms in which dual-purpose lighting is used.

Pfund⁹⁰ estimated the coefficients of diffused reflection from dry pigment surfaces by calculation from photographic records obtained by allowing the light reflected by a pigment surface from a small quartz mercury arc to enter the slit of a small concave grating spectrograph. When light falls on a thick layer of fine particles it penetrates a large number of particles before being returned, so that the reflection coefficients give roughly qualitative results for the opacities of the pigments examined. Zinc oxide became practically opaque near 3600Å; basic carbonate white lead was by far the most transparent pigment examined. "Titanox," Timonox, lithopone, and sublimed white lead fell between these limits. Powdered sulfur is very opaque. Fused magnesia has constant reflecting power throughout the ultraviolet spectrum. In general, sulfur and zinc oxide are the most effective pigments in removing radiations harmful to the film. The inerts are the least effective. From studies of mixtures with a volume ratio of pigment to vehicle of 1:60 in films 0.065 mm. thickness, determinations of the decreased transmission due to pigment placed the transparencies of the pigments in the same relative positions as the determination of the diffused reflection coefficients. The transmission of the inert pigments is very high and is nearly non-selective.

Hallett⁹¹ attacked the same problem in a somewhat different manner. The light from a quartz mercury lamp, after passing through a suitable glass filter to remove practically all the visible spectrum, passed through a quartz lens onto the painted surface from which it was either reflected or transmitted to sensitized paper.

⁸⁶ van Hoek, C. T., *Farben Ztg.*, **34**, 833, 895, 954, 1006 (1929); *Brit. Chem. Abs.*, **B**, 180 (1929).

⁸⁷ Wagner, H., *Farben Ztg.*, **34**, 2011 (1929); *Brit. Chem. Abs.*, B565 (1929).

⁸⁸ Zhukova, A., and Sovalova, A., *Za Lakrasochnuyu Ind.*, No. 2, 11, 1934; *Chem. Abs.*, **29**, 3859 (1935).

⁸⁹ Barker, J., *Oil, Colour Trade J.*, **87**, 575 (1935); *Chem. Abs.*, **29**, 7675 (1935).

⁹⁰ Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 369 (1923).

⁹¹ Hallett, R. L., *Proc. Am. Soc. Testing Materials*, **23**, II, 379 (1923); *Chem. & Met. Eng.*, **29**, 64 (1923).

The paper was developed and the degree of blackening determined by measurements with a Howland color photometer, and calculated to the "Arturascale," in which the unexposed paper is taken as zero and the completely exposed paper as 100 per cent black. The values in per cent reflected, transmitted and absorbed by paints containing the following pigments (all in the same volume relation to the vehicle) are: Basic carbonate white lead, 42, 4, 54; zinc oxide, 0, 0, 100; basic sulfate white lead, 3, 0, 97; Titanox, 16, 0, 84; lithopone, 36, 1, 63; red lead, 1, 0, 99; iron oxide, 1, 0, 99; lamp black, 2, 0, 98. Further observations are due to Stutz.⁹² New,⁹³ however, finds it impossible to predict from the transmission and reflection coefficients of pigments their effect on the durability of paint films exposed to ultraviolet radiation. In general, white paints are superior to aluminum paints in reflecting sunlight and in cooling power. Wagner and Pabst⁹⁴ find even thick films of white lead highly translucent to visible and ultraviolet light. Red lead is also transparent in thin but not in thicker layers. The addition of 50 per cent barite increases the translucency about 20 per cent. Finely dispersed hammerscale or lead reduction scale renders films opaque. Zinc white, so-called molybdate red lead, and iron oxide with zinc white or zinc chromate impart ultraviolet opacity.

The possibility exists that a pigment which absorbs energy may become excited thereby and may then pass over some of this energy of excitation to the film components. Goodeve⁹⁵ states that zinc and titanium oxides, which exhibit a steep fall in reflecting power at 3850 and 4000 Å, may serve as sources of photoactivation for the oxidation of oil vehicles or for the bleaching of adsorbed dyestuffs. He finds, however, that zinc oxide does not cause the oxidation of linseed oil, although titanium oxide does. The reduction of chalking by zinc oxide is a specific effect, attributed to internal filter action. Goodeve has also given the diffuse reflecting power of other materials such as lead carbonate, barium sulfate, magnesium carbonate and silica.

Luckiesh and Holladay⁹⁶ state that casein and nitrocellulose lacquer can be used as binders for ultraviolet reflecting paints, and that these should preferably contain a large proportion of magnesite, magnesium carbonate, alumina, or a mixture of these. Moderate amounts of silica, calcium carbonate, china clay and asbestos may be added without greatly reducing the reflecting power, which is about 5 to 65 per cent.

Lighting by luminous paints is proposed by Risler.⁹⁷ A surface coated with a luminous paint containing a phosphorescent sulfide is rendered continuously luminous by subjecting it to the rays of the spectrum ranging from blue to ultraviolet. To obtain the rays, a vacuum tube activated by high-frequency currents and filled with gas, such as nitrogen, argon or air, is preferably used. In a modification of the process,⁹⁸ a vacuum tube with or without electrodes and filled with rarefied gas such as argon, nitrogen or air is coated internally or externally with a luminous paint containing a phosphorescent sulfide, or having the sulfide incorporated in the glass of the tube, whereby a continuous luminous effect is obtained. The sulfides may be mixed with a varnish and the luminous coating is preferably covered with an impermeable and fireproof coating comprising cellulose acetate, alcohol, triacetin, acetone and tetrachloroethane (see also Chapter 8).

⁹² Stutz, G. F. A., *J. Frank. Inst.*, 200, 87 (1925); 202, 89 (1926); *Ind. Eng. Chem.*, 19, 897 (1927).

⁹³ New, G. F., *J. Oil and Colour Chem. Assoc.*, 19, 156 (1936); *Chem. Abs.*, 30, 8652 (1936).

⁹⁴ Wagner, H., and Pabst, E., *Farben Ztg.*, 42, 664, 691 (1937); *Chem. Abs.*, 31, 8952 (1937); Kessler, *Farben Ztg.*, 43, 39 (1938); *Chem. Abs.*, 32, 4360 (1938).

⁹⁵ Goodeve, C. F., *Trans. Faraday Soc.*, 33, 340 (1937).

⁹⁶ Luckiesh, M., and Holladay, L. L., *J. Frank. Inst.*, 212, 787 (1931); *Chem. Abs.*, 26, 5218 (1932).

⁹⁷ Risler, J., *British P.* 207,786, 1923.

⁹⁸ Risler, J., *British P.* 208,723, Dec. 20, 1923.

SYNTHETIC RESINS

Before discussing the applications of ultraviolet in the preparation and testing of varnishes, the relations of radiations to the artificial resins will be considered.⁹⁹ Some polymerization reactions employed in the preparation of vinyl resins have been mentioned in Chapter 23. Ramstetter¹⁰⁰ carried out the condensation of carbamide or its derivatives and formaldehyde under the influence of radiation of short wave-lengths, *e.g.*, from a quartz mercury lamp, in the presence or absence of condensing agents. The rays were applied during the whole or part of the reaction or during the concentration of the reaction solution or the hardening of the product. In one example, a solution of carbamide is treated at 75°C. with a mixture of 80 per cent formic acid and 30 per cent formaldehyde at 40°C. and heated for a quarter hour under reflux while being irradiated. Excess of formaldehyde is distilled off under reduced pressure at 40°C. till a syrup remains and the latter is poured into flat molds. On keeping, it finally forms transparent flexible flakes, the hardening process also being accelerated by exposure to ultraviolet light. Geisel¹⁰¹ states that the hardening is accelerated and that a tendency to cloud or deposit is counteracted if the mass is subjected to the action of ultraviolet light. Shono¹⁰² found a phenol-formaldehyde resin to be decolorized in proportion to the amount of the ultraviolet rays (3190-2585Å) to which it was exposed. Most resins made from the condensation products of phenols and aldehydes present the difficulty of discoloration by light. The urea-formaldehyde resin has, however, been found relatively light-stable.¹⁰³

A substitute for drying oils as a medium for paints, varnishes, and impregnating agents for fabrics, wood, etc., proposed by Röhm,¹⁰⁴ consists of a solution of polymerized acrylic acid ester in acetone, lower fatty acids or other solvents. When exposed to sunlight or ultraviolet light, the ester is transformed into a colorless, transparent, tough mass, soluble in solvents for oils.

The polymerization of the methacrylates is furthered by heat, light, oxygen and peroxides. These resins have extreme ultraviolet transmission and excellent light stability.¹⁰⁵ Wave-lengths shorter than 2200Å decompose methyl-methacrylate vapor, but longer ones polymerize it to a white solid. Once started by light, the polymer continues to grow in the dark for several days. This growth is proportional to the area of the tube irradiated and the pressure of the vapor.¹⁰⁶

Furfural resins have a good black color and completely absorb ultraviolet rays. By adding a suitable amount of Bakelite resin, they can supply a very fine ebonite-like insulating material or an effective coating varnish which protects ebonite from ultraviolet rays.¹⁰⁷

In preparing lacquers in which a resin fast to sunlight or ultraviolet light is

⁹⁹ Fluorescence tests for the identification of resins have been tabulated by Wagner and Schirmer. Wagner, H. and Schirmer, H., *Farben Ztg.*, 43, 131, 157 (1938); *Chem. Abs.*, 32, 4361 (1938).

¹⁰⁰ Ramstetter, H., German P. 416,252, Jan. 31, 1923; *Brit. Chem. Abs.*, B, 99 (1926).

¹⁰¹ Geisel, W., German P. 437,646 (1924); *Brit. Chem. Abs.*, B, 452 (1927).

¹⁰² Shono, T., *J. Soc. Chem. Ind. Japan*, 30, 143 (1927); see also *Chem. Abs.*, 20, 2729 (1926).

¹⁰³ Ellis, C., *Chem. Met. Eng.*, 16, 1928; for the use of a sun lamp in testing the durability of color in brightly colored urea resins, see Houwink, R., *Trans. Inst. Plastics Ind.*, 5, No. 9, 16; *Chem. Abs.*, 30, 3905 (1936).

¹⁰⁴ Röhm, O., German P. 295,340, June 5, 1915; *J. Soc. Chem. Ind.*, 296 (1917).

¹⁰⁵ E. I. du Pont de Nemours & Co., *Ind. Eng. Chem.*, 28, 1160 (1936); Barrett, H. J., and Strain, D. E., British P. 465,789, May 14, 1937; *Chem. Abs.*, 31, 7444 (1937); Plauson, H., (Rohm and Haas Co.), U. S. P. 2,086,093, July 6, 1937; *Chem. Abs.*, 31, 5811 (1937); Chalmers, W., U. S. P. 2,087,468-9, July 20, 1937; *Chem. Abs.*, 31, 6378 (1937).

¹⁰⁶ Melville, H. W., *Proc. Roy. Soc.*, A163, 511 (1937); *Brit. Chem. Abs.*, 1938A, 261.

¹⁰⁷ Ogawa, W., Hanyu, T., and Yanagihashi, T., *Researches Electrotech. Lab., Tokyo*, No. 178, 78 pp. (1926); *Chem. Abs.* 21, 659 (1927).

required, Moss and White¹⁰⁸ employ synthetic aniline (or other amine)-furfural resins, adding these to lacquers containing one or more derivatives of cellulose, such as cellulose nitrate, acetate, etc., and a volatile organic solvent, other natural or semi-synthetic resins, plasticizers, pigments or dyes. Phenol or ketone furfural resins also may be used.¹⁰⁹

Most of a series of synthetic and natural resins and gums studied by Gamble and Stutz¹¹⁰ tended to decompose in ultraviolet light. This change was accompanied by a yellowing and an increase in the ultraviolet absorption coefficients. Ester gum was classified as being relatively opaque and also relatively stable to these radiations.

In general, the resinous materials are both more opaque and less sensitive to ultraviolet light than are the oleoresinous or nitrocellulose films. Incorporation of a resin therefore affords a certain degree of protection to such sensitive materials. The most desirable type of resin to use would be one which is both opaque and stable to these rays, but there are only a few such resin esters such as Congo, manila and rosin. It is also necessary to consider other factors, such as the physical and chemical properties of the resin and its resistance to weathering. Certain synthetic resins may have a chemical stabilizing action on nitrocellulose even though their own ultraviolet absorption characteristics may be undesirable. The phenol-formaldehyde, glycerol-phthalic anhydride and coumarone-indene types are fairly satisfactory. These all exhibit about the same high opacity, but differ in their sensitivity to the ultraviolet, the coumarone-indene group being the most readily decomposed. In general, the natural gums and resins are both less sensitive and more transparent than are the synthetic materials. Kauri gum was found to be the most stable of the natural resins measured. Vinyl acetate and vinyl chloride have high transparency but are considerably decomposed. A mixture of polymerized vinyl acetate and chloride is both more opaque and less sensitive than vinyl acetate alone.

With a view to obtaining photographic films more transparent than gelatin to the short ultraviolet rays, Dote and Shidei¹¹¹ measured the absorption of films from solutions of agar agar and of commercial viscose films. The films were more transparent than the corresponding solutions, which were themselves more transparent than gelatin especially in the extreme ultraviolet.

Minor¹¹² has employed ultraviolet for bleaching rosin. On the other hand, coumarone resin¹¹³ is darkened on exposure to an ultraviolet lamp for three hours at a distance of a few inches.

The solubility of colored resins submitted to the action of light has been investigated by des Bancel.¹¹⁴ Colored resins were prepared by treating resin with aqueous solutions of alkali hydroxides, adding a suitable coloring matter (safranin, rhodamine, etc.) and then precipitating with a salt of zinc or magnesium. These resinous substances, when dissolved in a volatile solvent, spread in a thin layer on glass plates, dried and exposed to a mercury-vapor lamp, became,

¹⁰⁸ Moss, W. H., and White, B. B., British P. 307,290, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 23, 5338 (1929).

¹⁰⁹ Moss, W. H., and White, B. B., British P. 307,291, 307,289, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs.*, B, 469 (1930).

¹¹⁰ Gamble, D. L., and Stutz, G. F. A., *Ind. Eng. Chem.*, 21, 330 (1929).

¹¹¹ Dote, S., and Shidei, T., *Japan J. Physics*, 5, 157 (1929); *Brit. Chem. Abs.*, A, 661 (1930).

¹¹² Minor, L. C., U. S. P. 939,733, Nov. 9, 1909; *Chem. Abs.*, 4, 521 (1910).

¹¹³ Ellis, C., and Rabinovitz, I., *J. Ind. Eng. Chem.*, 8, 800 (1916).

¹¹⁴ des Bancel, L., *Compt. rend.*, 155, 280 (1912); *J. Chem. Soc.*, 102 (II), 882 (1912).

at the end of a certain time. insoluble in such solvents as benzene, but soluble in methyl or ethyl alcohol.

According to Chinchin,¹¹⁵ the action of sun and electric rays on rosin causes the formation of a more stable form, insoluble in petroleum ether, having a different dielectric constant and resulting in a molecular agglomeration.¹¹⁶

The colloidal condition of stearates, palmitates and oleates of copper, aluminum, zinc, calcium and other water-insoluble soaps is affected adversely and their solubility is impaired by ultraviolet irradiation.¹¹⁷

VARNISHES AND LACQUERS

Wolff¹¹⁸ believed the shrivelling observed to occur in varnishes dried in red light due to a slight retardation by the rays of the surface oxidation, and a greater retardation of polymerization in the inner layers. In light of shorter wave-lengths the processes were thought to proceed at nearly equal rates. Vollmann¹¹⁹ believes the red rays cause an unequal distribution of heat which influences polymerization in the inner layers.

In the laboratory of the senior author, a large number of samples of varnishes of various grades have been exposed to ultraviolet rays. The behavior of varnishes varies greatly, depending on the composition. Some samples are bleached, others are darkened and still others are very little altered in color.

In the application and treatment of varnish, Clover¹²⁰ conveys the varnished articles through a chamber exposed to heat and to light rich in ultraviolet rays.

Ultraviolet accelerated weathering tests have been extensively used for varnishes, lacquers and enamels. Mougey¹²¹ was unable to find a direct relationship between the results of these and of service tests when different types of materials were compared. In early tests made by Mougey on black baking fender enamel, panels failed on the test rack before they did under direct ultraviolet irradiation. When the panels were soaked in water over night and exposed to the ultraviolet during the day, they failed in a few days, but the results were of no value unless care was taken to remove surface water. Failure occurred in a few minutes at the areas where surface water lay on the panels. Finishing varnishes subjected to this test usually failed in one cycle, with no relation between the results of the test and the durability of the varnish. It was apparent that this test favored hard-drying finishes. A rotating wheel type of apparatus was used, half immersed in water and rotating at a rate of two revolutions per hour under the ultraviolet lamp. In this way the panels supported on the wheel were given time for drainage and evaporation of surface moisture and then exposed. A Duco nitrocellulose enamel which withstood exposure on the roof test rack for over two years failed in two days in this test. A finishing varnish with a life of three months on the

¹¹⁵ Chinchin, I., *Bumazhnaia Promyshlennost*, No. 12 (1924); *Chem. Abs.*, 19, 2273 (1925).

¹¹⁶ For extinction coefficients of crude and bleached Japan wax, see Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, 38, 218 (1935); *Chem. Abs.*, 29, 5296 (1935). Crude wax showed a remarkable absorption at 6600Å. Sunlight bleaching is facilitated by extraction of the pigment with alcohol. Sakuma, I., Momose, I., and Shomura, J., *J. Soc. Chem. Ind. Japan*, 40, 48 (1937); *Chem. Abs.*, 31, 6042 (1937); Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, 40, 170 (1937); *Chem. Abs.*, 31, 6495 (1937).

¹¹⁷ Jones, H. I., *Chem. Met. Eng.*, 28, 489 (1923); *J. Soc. Chem. Ind.*, 42, 410A (1923).

¹¹⁸ Wolff, H., *Farben Ztg.*, 24, 1119, 1389 (1919); *J. Chem. Soc.*, 115, 915A; see, however, Ragg, M., *Farben Ztg.*, 24, 1308 (1919).

¹¹⁹ Vollmann, H., *Farben Ztg.*, 24, 1427 (1919).

¹²⁰ Clover, G. R., U. S. P. 1,646,010, Oct. 18, 1927; *Brit. Chem. Abs.*, B, 916 (1927).

¹²¹ Mougey, H. C., *Ind. Eng. Chem.*, 17, 412 (1925); see also Jenkins, L. D., and Croll, P. R., *Ibid.*, 19, 1356 (1927).

roof test would stand two or three weeks on the wheel. Apparently, there was no connection between the results of the test and the life of finishing materials on the roof test rack. The results were better when the wheel was continuously rotated day and night and the lamp used only during the day.

Wolff and Zeidler¹²² prepared test films of the coating material on a colored gelatin film glued on paper strips. When dry, the film was placed with the coated side on a glass plate, and the gelatin removed with water at 50°C. It is then tested for tensile strength, elasticity and elongation. A kauri varnish film after exposure to the light of a quartz lamp showed an increased extension velocity.

Hansen¹²³ described a very simple and comparatively inexpensive test in which panels 2.5×13 cm. are exposed in a shallow pan under a source of ultraviolet light. By means of an intermittent siphoning apparatus, the panels are periodically covered with water and allowed to dry out. A cycle of one and one-half hours dry and one-half hour wet exposure was used, but the method when published had not yet been standardized with materials of known characteristics. Tognoni and Trolliet report favorable results with the Weather-Ometer.¹²⁴

von Mühlendahl and Schulz¹²⁵ rotate a vertical wheel partly immersed in water, once in fifteen minutes. One day in this test is said to produce results closely paralleling one month of weathering.¹²⁶

An embrittling test for predicting the durability of varnishes was devised by Wilson.¹²⁷ In it, varnish films on metal strips are exposed to a carbon arc or to Mazda lamps at a distance of 15 inches until they are so affected that they crack or whiten on bending double at 0 or 22°C. over a 3 mm. rod. The time of exposure to light required to produce this effect is taken as a measure of durability. Levy¹²⁸ found that this test, although valuable for classifying good and poor grade varnishes, would not rapidly distinguish grades of the newer types of synthetic resin coatings. An improvement by which the coatings are applied to surfaces of rubber sheeting that can be stretched instead of bent is suggested to make observation easier. Snitter¹²⁹ used a flexometer in which the test panel is gradually bent, the line at which bending is effected being observed under a magnifying glass. The angle at which fissuring of the varnish film occurs is noted. He did not find that artificial aging methods give results comparable to the effects of exposure to the weather.¹³⁰

Nitrocellulose Lacquers. Particular attention has been devoted to the light-stability of the newer types of coatings. Stutz¹³¹ made ultraviolet absorption studies of lacquer films, noting particularly the effects of the addition of plasticizers and gums. In general, the light penetrates some distance into the film before being completely absorbed. Similar data on films of acetylcellulose, both pure and plasticized with tritolyl phosphate and *p*-toluenesulfonanilide have been

¹²² Wolff, H., and Zeidler, G., *Farben Ztg.*, **32**, 2135, 2708 (1927); *Chem. Abs.*, **22**, 1860 (1928).

¹²³ Hansen, H. V., *Ind. Eng. Chem.*, **20**, 1384 (1928).

¹²⁴ Tognoni, C. A., and Trolliet, A. L., *Chimie & Industrie*, **38**, 647 (1937); *Chem. Abs.*, **32**, 3642 (1938).

¹²⁵ von Mühlendahl, E., and Schulz, H., *Z. angew. Chem.*, **40**, 1185 (1927).

¹²⁶ For a description of a wheel developed by the Ditzler Co., see Denham, A. F., *Automotive Industries*, April 9, 1927.

¹²⁷ Wilson, J. H., *Bureau Standards J. Research*, **7**, 73 (1931).

¹²⁸ Levy, S. A., *Am. Paint Varnish Mfrs. Assoc. Circular* **410**, 146 (1932); *Chem. Abs.*, **26**, 3939 (1932).

¹²⁹ Snitter, P., *Bull. inst. pins*, 223 (1933); *Chem. Abs.*, **28**, 1554 (1934).

¹³⁰ See also Martin, R. C., *Metal Cleaning and Finishing*, **6**, 561 (1934).

¹³¹ Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1235 (1926).

given by Orlova.¹³² Data are reported by Nakashima and Negishi¹³³ for various cellulose films as altered by swelling and softening agents.

The viscosity of nitrocellulose solutions decreases on exposure to light.¹³⁴ The colloidal changes occurring in nitrocellulose collodion with time and under the influence of ultraviolet light have been studied by Breguet¹³⁵ by fractional precipitation of the nitrocellulose by the method of Duclaux and Wollmann, using benzene instead of water to prevent precipitation of the camphor. The weight, viscosity and nitrogen content of the various fractions was determined. The results were interpreted in terms of the Duclaux theory of the constitution of reversible gels as follows: In a collodion the most complex nitrocellulose molecules have the greatest tendency to polymerize and swell, and in a nitrocellulose solution the solid phase is formed of the largest granules, the cells of which are filled with a dispersion of the finer granules of the solvent. The granules of collodion are in equilibrium with the solvent, and in time the cohesion forces of the molecules in the granules gradually diminish, and the granules are progressively depolymerized with resulting decrease in swelling, made evident by decreased viscosity. This aging does not proceed indefinitely but tends to a limit which depends on the concentration, temperature, and nature of the nitrocellulose collodion. Aging is accelerated by heat, light and mechanical treatment. The changes taking place in collodion with time are thus due to its changing from an emulsoid to a suspensoid. The general effects of ultraviolet light on celluloid or collodion are to lower the viscosities of all fractions and to decrease the total yield of high-viscosity nitrocellulose and correspondingly increase the yield of low-viscosity nitrocellulose.

Branchen and Prachel¹³⁶ proposed to make practical application of the ability of ultraviolet light to reduce the viscosity of an acetone solution of cellulose acetate in the presence of a fatty acid, preferably formic or acetic. In fifty hours a viscosity ranging from one-half to one-fifteenth that of the original value may be obtained.

During degradation by ultraviolet rays the tensile strength of cellulose acetate films with the same acetyl numbers varies as the viscosity. The stretch varies similarly but to a greater degree.¹³⁷ During this form of aging of a film base, there is associated with the depolymerization of the ester (shown by the decrease in viscosity) an increase in brittleness and a yellowing.¹³⁸

When employed in layers in safety glass, nitrocellulose has been found to be light-sensitive, decomposing on prolonged exposure to light. Cellulose acetate promised better results as it is more stable, but it is still not ideal for the intermediate layer.¹³⁹

It has been claimed that the instability toward light of nitrocellulose films depends on impurities introduced during preparation.¹⁴⁰ The most harmful impuri-

¹³² Orlova, O. V., *J. Tech. Physics, U.S.S.R.*, 4, 1170 (1934); *Chem. Abs.*, 29, 8321 (1935).

¹³³ Nakashima, T., and Negishi, M., *J. Soc. Chem. Ind. Japan*, 39, Suppl. binding, 102, 104 (1936); *Chem. Abs.*, 30, 5407 (1936).

¹³⁴ McBain, J. W., Harvez, C. E., and Smith, L. E., *J. Phys. Chem.*, 30, 312 (1926); *Chem. Abs.*, 20, 1741 (1926).

¹³⁵ Breguet, A., *Rev. gen. colloides*, 3, 200, 230 (1925); *Chem. Abs.*, 19, 3590 (1925). See also Rogovin, Z. A., and Glazman, S., *J. Gen. Chem. (U.S.S.R.)*, 8, 498 (1938); *Chem. Abs.*, 32, 7260 (1938).

¹³⁶ Branchen, L. E., and Prachel, C. U., U. S. P. 1,658,368, Feb. 7, 1928, to Eastman Kodak Co.; *Chem. Abs.*, 22, 1237 (1928).

¹³⁷ Grard, J., *Bull. soc. chim.*, 53, 1308 (1933); *Chem. Abs.*, 28, 4222 (1934).

¹³⁸ Kozlov, P. V., and Zueva, R. V., *Photo-Kino Chem. Ind. (U.S.S.R.)*, No. 5, 14, 1935; *Chem. Abs.*, 30, 4107 (1936).

¹³⁹ Ellis, C., *Chem. Met. Eng.*, 16 (1928).

¹⁴⁰ Mindlin, S. S., Zel'dovich, P. Y., Kaplan, M. Y., Kuz'mina, L. I., and Remennikova, V. S., *Plasticheskie Massui*, No. 4, 4, 1934; *Chem. Abs.*, 29, 3154 (1935).

ties are ferrous salts, ferric salts being less so. Extraction of the nitrocellulose with hydrochloric acid can remove most of the iron salts. Decomposition products of cellulose, organic acids, aldehydes and sodium hypochlorite used for bleaching have no effect, but copper salts are also harmful. The photochemical stability is independent of the temperature of nitration and the thermal stability.

Callahan¹⁴¹ stated that a clear film of cellulose nitrate exposed to the ultraviolet rays of the sun's spectrum for only a few days becomes so brittle that it will not stand bending without cracking. The use of oils and plasticizers will extend this life but eventually failure will occur. However, if such a film is protected from the sun's rays by the use of opaque pigments, particularly when the film is applied to a rigid surface such as steel, almost indefinite resistance to sunlight will result. Scheiber¹⁴² attributes the brittleness produced by light to the possibility of crystallization of the cellulose esters. In the absence of pigment, plasticizer and resin, ultraviolet light causes in nitrocellulose films a yellowing when wetted by 10-per cent sodium hydroxide, an increase in the wettability by water and ethyl acetate, an acid reaction and an unpleasant odor. The changes may be the result of saponification following the production of free organic acids.¹⁴³ Kraus¹⁴⁴ believes that the degree of yellowing in nitrocellulose lacquers depends on the nature and concentration of the plasticizer as well as on the exposure.¹⁴⁵

It has been found¹⁴⁶ that the absolute intensity of yellowing of nitrocellulose films with 33.3 per cent tritoly phosphate as plasticizer, when exposed to a mercury arc, was greater for 135 μ films than for 15 μ films. But when expressed as amount of yellowing per unit thickness, the change was greater in the thinner films. The amount of additional yellowing decreases for each added increment of time.

Kraus¹⁴⁷ finds that ultraviolet greatly impairs the plasticity imparted to nitrocellulose by butyl oleate or benzyl stearate. Palatinol AS and Palatinol L are superior. Irradiation caused strong yellowing with Toplast, somewhat less with benzyl stearate and very little with Palatinol AS, Palatinol L and butyl oleate.

Nishizawa¹⁴⁸ follows the rate of decomposition of nitrocellulose by light by determining nitrogen dioxide with α -naphthylamine. Kraus, however, did not believe the destruction of the film to be simply related to either the degree of denitration or to the loss of the solubility in acetone. Although the ability of the plasticizers to combine with the nitrogen decomposition products had an influence on the characteristics, direct relations could not be discerned.

Attempts have been made to increase the stability of nitrocellulose films to sunlight, i.e., to decrease their chalking, by the introduction of pigments. McKim¹⁴⁹ prepared a clear cotton solution and in this ground a small amount of zinc oxide to determine whether a pigment opaque to ultraviolet light exerted a protective

¹⁴¹ Callahan, M. J., *Chem. & Industry*, 47, 34, 236T (1928).

¹⁴² Scheiber, J., *Farbe und Lack*, 190 (1928); *Chem. Abs.*, 22, 3054 (1928).

¹⁴³ Beutel, E., and Kutzelnigg, A., *Farbe und Lack*, 351 (1934); *Brit. Chem. Abs.*, B, 804 (1934); see also Gloor, W. E., *Ind. Eng. Chem.*, 23, 980 (1931).

¹⁴⁴ Kraus, A., *Paint Varnish Production Mfr.*, 13, 16, 18 (1935); *Chem. Abs.*, 30, 307 (1936); *Farbe und Lack*, 545, 556 (1935); *Chem. Abs.*, 28, 891 (1934).

¹⁴⁵ A general discussion of the aging of oil, gum, resin and cellulose derivatives under the influence of light and air and of the effects of pigments upon it has been given by Nautoy, A., 14 *Congr. chim. ind. Paris* (Oct. 1934); *Chem. Abs.*, 29, 6443 (1935). Note also Rosenthal, L., and Schultze, G., *Farben-Chem.*, 53 (Feb., 1934); *Synthetic and Applied Finishes*, 65 (June, 1934).

¹⁴⁶ Communication III from the Untersuchungs- und Forschungs Laboratorium für Lacke und Farben, Berlin, *Farben-Ztg.*, 42, 667 (1937); *Chem. Abs.*, 31, 8960 (1937); Wolff, H., and Zeidler, G., *Paint Varnish Production Mfr.*, 17, 7, 10 (Sept., 1938); *Chem. Abs.*, 32, 7162 (1938).

¹⁴⁷ Kraus, A., *Farbe und Lack*, 269 (1938); *Chem. Abs.*, 32, 8806 (1938).

¹⁴⁸ Nishizawa, Y., *J. Chem. Soc. Japan*, 50, 258, 327, 391 (1929); *Chem. Abs.*, 25, 5627 (1931).

¹⁴⁹ McKim, W. A., *Ind. Eng. Chem.*, 18, 1239 (1926); de Waele, A., *J. Soc. Dyers Colourists*, 43, 42 (1927).

action. The reduction in distensibility produced by an ultraviolet exposure, which in the clear film caused a destruction of 100 per cent, was in this way reduced to but 60 per cent. The breaking strength of the clear film increased from 9 to 18 units and in the pigmented film from 30 to 36.

For the protection of automobile finishes, Denham¹⁵⁰ found a fairly large amount of pigment necessary. Although opaque colors in general stood up better than those of lower opacity, some, notably the Para toners, did not furnish as much protection. Although more opaque than madder lakes, they made up into less durable lacquers. White pigments (titanium, lithopone, zinc oxide) are very durable but zinc sulfide is undesirable, since it turns brown on exposure. Ultramarine lacks durability, since it does not provide protection against actinic rays. Of true lake colors, alizarin pigments produce the most durable so-called lake colors in pyroxylin lacquers. Since they have poor covering qualities, they must be strengthened with other materials which detract from durability.

In discussing accelerated weathering of lacquer enamels, Nelson¹⁵¹ noted that it is possible to produce such failures as hair-line checking by increasing the oxygen content of the air in the light-exposure chamber and by including periodic exposure to humid air containing sulfur dioxide and carbon dioxide. He believed the relative ratings of a series of nitrocellulose lacquers in this test agreed reasonably well with outdoor exposure ratings.

Pigmented enamels made with cottons of higher viscosity showed greater durability and greater tensile strength and distensibility than those made with 0.5-second cotton. This may be due to the longer fibers used in the production of the cottons of higher viscosity, or to the freedom from suspended matter usually present in the solutions of the latter. Greater durability resulted from a ternary mixture containing 50 per cent of 0.5-second cotton, 24 per cent of 4-second cotton and 26 per cent of leather dope. The last by itself showed the poorest durability of all the cottons tested.

In weathering, light-colored enamels containing 19.5 per cent of 0.5-second cotton yellowed more than those containing 16 per cent of the same cotton; the former, containing pigment transparent to ultraviolet light, were more durable than the latter, but with pigments opaque to ultraviolet light, the enamels containing the lower cotton content were the more durable. Increasing the gum content from 1.5 to 3 per cent decreased durability and increased gloss when dammar gum was used, but with ester gum both these properties were increased. Comparative tests of tricresyl phosphate and triphenyl phosphate showed little preference except when the tests were run at 48°C., when the films containing the latter rapidly became weak and brittle, apparently as a result of crystallization of the plasticizer. The addition of clear lacquer to a pigmented lacquer in the finishing coats, or a finishing coat of clear lacquer or of varnish, always decreased the durability of the pigmented lacquer job. A wax finish stands up better than a buff finish.

Von Mühlendahl and Schulz¹⁵² studied the influence of plasticizers on nitrocellulose under the influence of light and heat, judging it from the color of a mixture of equal amounts of the two products when heated to 100°C. or exposed to the rays of a quartz lamp.

According to Merz,¹⁵³ weathering under a carbon arc, and the results of a

¹⁵⁰ Denham, A. F., *Automotive Industries*, 56, 544 (1927).

¹⁵¹ Nelson, H. A., *Can. Chem. Met.*, 10, 11 (1926); *Chem. Abs.*, 20, 995 (1926).

¹⁵² Von Mühlendahl, E., and Schulz, H., *Farbe und Lack*, 276 (1927); *Chem. Abs.*, 22, 3055 (1928).

¹⁵³ Merz, O., *Farben Ztg.*, 36, 316, 362 (1930); *Chem. Abs.*, 25, 608 (1930).

baking-bending test of a series of red, white and black lacquers with varying quantities of ester gum, gave the best correlation with outside weathering.

Studies of the ultraviolet light absorption by lacquer films and their constituents indicated that within the range present in sunlight, all of the absorption by an ordinary lacquer is due to ester gum with lesser absorption by such plasticizers as tricresyl phosphate and castor oil.¹⁵⁴ The failure of ordinary lacquer films is ascribed to excited ester gum molecules transferring their energy to neighboring nitrocellulose molecules. Avoidance of the use of ingredients opaque to the ultraviolet of sunlight should improve the light resistance. In general agreement with this, Münzinger¹⁵⁵ observed that nitrocellulose films containing 29 different softeners were all more sensitive than the nitrocellulose alone. Castor oil and tritolyl phosphate caused the greatest and glycol monomethylphthalate the least alteration on exposure. Münzinger also tabulated the changes in fluorescence colors resulting from the exposure.

The Elektrizitätswerk Lonza¹⁵⁶ produces a varnish containing diphenylamine to retard the absorption of ultraviolet light by nitrocellulose films.

Dykstra¹⁵⁷ uses crotyl cellulose or allyl cellulose and a drier, such as cobalt oleate, for lacquers which may be baked. Ultraviolet light may be used for insolubilizing the films of crotyl cellulose. Ethylcellulose films approximate acetylcellulose films in transparency and light resistance. Prolonged exposure of ethylcellulose films to ultraviolet light at high temperatures depolymerizes the cellulose molecule with lowering of the viscosity.¹⁵⁸

Since the cellulose acetate lacquers are more resistant to light than cellulose nitrate lacquers, it has been proposed to coat the latter with the former.¹⁵⁹ However, cellulose acetate does not absorb the rays which decompose the nitrate in the lower layers so that such protection is not complete. To overcome this, many additions to the cellulose acetate layer have been suggested to render them opaque. The addition of 7 oz. of stannic acid per gallon has been proposed for use in protective coatings for airplane wings by Doerflinger. In the preparation of an actinism-proof cellulose ester composition, Clewell¹⁶⁰ coats transparent sheets of pyroxylin on both sides with a colorless transparent oil-resin varnish, *e.g.*, a copal-linseed oil mixture impervious to ultraviolet light.

In the cellulose acetate of other overcoatings, Staud and Murray¹⁶¹ use about 2 per cent of phthalic acid neutral esters of monoethers of hydroquinone and their homologs. In the production of laminated glass, two layers of overcoating are placed on each side of the cellulose nitrate film which is then incorporated between two sheets of glass. (It was also claimed that crystallization within the cellulose ester sheets produced beautiful effects and that such materials might be useful in the manufacture of toilet articles, novelties, etc.)

Many other organic substances have been proposed for this purpose, including polycyclic hydrocarbons or their derivatives, such as phenanthrene, naphthalene,

¹⁵⁴ Davey, W. P., Duncan, D. C., and Wiggam, D. R., *Phys. Rev.*, **35**, 1423 (1930); *Ind. Eng. Chem.*, **23**, 904 (1931).

¹⁵⁵ Münzinger, W. M., *Chem. Ztg.*, **56**, 851 (1932).

¹⁵⁶ Swiss P. 128,476, May 25, 1927, to Elektrizitätswerk Lonza; *Chem. Abs.*, **23**, 2840 (1929).

¹⁵⁷ Dykstra, H. B., U. S. P. 1,920,297, Aug. 1, 1933; *Chem. Abs.*, **27**, 4943 (1933).

¹⁵⁸ Ushakov, S. N., Shneer, I. M., Demina, E. N., and Ijboldina, *Rev. gén. mat. plastiques*, **13**, 341 (1937); *Chem. Abs.*, **32**, 3603 (1938).

¹⁵⁹ Application of Steel, P. C., U. S. Serial No. 425, 353. Cited by Staud, C. J., and Murray, T. F., Jr., U. S. P. 1,950,907.

¹⁶⁰ Clewell, J. H., Jr., U. S. P. 1,647,435, Nov. 1, 1927, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **22**, 317 (1928).

¹⁶¹ Staud, C. J., and Murray, T. F., U. S. P. 1,950,907, March 13, 1934; *Brit. Chem. Abs.*, **B**, 161 (1935).

chloronaphthalene, anthracene or *p*-amino-benzoic acid, phthalimide, nitroanisole, nitrobenzene, quinaldine, benzyl benzoate, glycerol butyl phthalate and β -methoxymethyl phthalate, dibenzofuran, diphenylbenzene, diphenylguanidine, xanthidrol or phthalanil.¹⁶²

Vanadium, cerium or titanium salts of a half ester of phthalic acid,¹⁶³ as well as triphenyl compounds of antimony or bismuth have also been suggested for this purpose.¹⁶⁴ Dreyfus¹⁶⁵ used a topcoat of phenol-furfural resin. This resin film is dried and converted to the insoluble, infusible state by baking, exposure to sunlight or ultraviolet light. Bradshaw¹⁶⁶ incorporates an iron or cobalt salt of naphthenic acid or a resin acid. Organic or inorganic compounds of copper may be added to purified benzylcellulose used as a basis for transparent films, sheets or plastics to render them resistant to the action of light and heat.¹⁶⁷

According to Cofman and de Vore,¹⁶⁸ the wave-length most effective per quantum absorbed in causing the acid decomposition of nitrocellulose is about 3100Å. It was to prevent the passage of this wave-length that most of the materials listed above were introduced. The observation by Rayleigh that celluloid containing malachite green becomes red when exposed to sunlight may be explained as due to the action of the liberated nitrogen oxides on the dye. Trevy¹⁶⁹ finds the light-yellowing of celluloid films most intense under wave-lengths between 3000 and 3500Å.¹⁷⁰ Traces of metals may increase the yellowing. Duropfen lacquer 218 V of the firm of Kurt Albert is completely opaque to ultraviolet light of wave-lengths shorter than 4000Å even in thin layers. In the visible range, it transmits light increasingly toward the red end of the spectrum.¹⁷¹

¹⁶² British P. 371,901, Oct. 24, 1930, to Eastman Kodak Co.; *Chem. Abs.*, **27**, 3094 (1933); Staud, C. J., U. S. P. 1,958,683; *Chem. Abs.*, **28**, 4614 (1934); Murray, T. F., U. S. P. 1,958,711; *Chem. Abs.*, **28**, 4615 (1934); U. S. P. 1,976,359; *Chem. Abs.*, **28**, 7562 (1934); Canadian P. 339,837, March 6, 1934; U. S. Patent 2,043,805; Richardson, E., and Staud, C. J., U. S. P. 1,958,714-5, *British Chem. Abs.*, **B**, 278 (1935); U. S. P. 2,017,165; *Brit. Chem. Abs.*, **B**, 1109 (1936); Staud, C. J., and Murray, T. F., U. S. P. 1,994,596; *Chem. Abs.*, **29**, 3182 (1935); Kocher, N. S., U. S. P. 1,973,488; *Chem. Abs.*, **28**, 7043 (1934).

¹⁶³ Salzberg, P., U. S. P. 1,965,608; Canadian P. 333,043, June 6, 1933; *Chem. Abs.*, **27**, 4428 (1933).

¹⁶⁴ Murray, T. F., U. S. P. 1,969,473, *Chem. Abs.*, **28**, 6329 (1934).

¹⁶⁵ Dreyfus, C., U. S. P. 1,964,039, June 26, 1934; *Brit. Chem. Abs.*, **B**, 402 (1935).

¹⁶⁶ Bradshaw, H., U. S. P. 1,962,132; *Chem. Abs.*, **28**, 4904 (1934).

¹⁶⁷ French P. 795,880, March 24, 1936, to Soc. des usines chimiques Rhone-Poulenc, *Chem. Abs.*, **30**, 5690 (1936).

¹⁶⁸ Cofman, V., and de Vore, H. B., *Nature*, **123**, 87 (1929).

¹⁶⁹ Trevy, P., *Rev. gen. mat. plast.*, **13**, 60, 131 (1937); *Brit. Chem. Abs.*, **B**, 767 (1937).

¹⁷⁰ See also Report of Paint and Varnish Research Lab., Berlin, *Farben Ztg.*, **42**, 667 (1937); *Brit. Chem. Abs.*, **B**, 1088 (1937).

¹⁷¹ Heyne, G., and Schön, M., *Angew. Chem.*, **49**, 784 (1936); *Chem. Abs.*, **31**, 321 (1937).

Chapter 31

Rubber

The absorption of ultraviolet radiations by rubber dissolved in pure hexahydro-toluene has been studied by Scheibe and Pummerer.¹ (See Figure 127.) Of samples of rubber from latex treated with alkali, rubber from non-coagulated latex, and "sol-rubber," the curves of the latter were believed most closely to approximate the absorption of rubber hydrocarbon. Gutta-percha gave a curve of similar type. Kröger and Staude² found that isoprene and various samples of rubber exhibit only continuous absorption. Synthetic rubber made from isoprene is more transparent than isoprene itself in the same thickness. The transparency of both synthetic and natural rubber increases with stretching,³ presumably on account of some molecular change. Rubber vulcanized with sulfur chloride is much less transparent.⁴

POLYMERIZATION AND DEPOLYMERIZATION

Deresinized, colorless gutta-percha on exposure to ultraviolet light becomes more opaque and brittle, although still completely soluble in benzene.⁵ This change has been assumed to be due to a transformation into a crystalline form, the existence of which has been demonstrated microscopically. Kirchhof⁶ states that experiments by Porritt⁷ indicated that a benzene solution of rubber slowly changes to a gel on exposure to ultraviolet light. Kirchhof found that this could be observed only in a very small volume of solution. With larger volumes depolymerization apparently occurred with a lowering of the viscosity. There have been many subsequent observations of the reduction of the viscosity of rubber sols by ultraviolet light.⁸

During this alteration of the viscosity of crude rubber solutions, the molecular polarization is not markedly affected, according to Kambara.⁹ Garner¹⁰ found that the reduction in viscosity during irradiation occurred particularly in solutions from which oxygen was excluded. On evaporation, there was obtained a depolymerized rubber which readily absorbed oxygen. Ordinarily, however, light and air cause both an oxidation and an increase in tackiness as judged by changes in viscosity. Garner concluded that the effect of light is partly polymerization and partly depolymerization. The latter predominates in an ordinary atmosphere. In nitrogen with but little oxygen, the rubber is in part rendered insoluble. The relative effects of various antioxidants in retarding the decrease in viscosity of irradiated

¹ Scheibe, G., and Pummerer, R., *Ber.*, **60**, 2163 (1927).

² Kröger, M., and Staude, H., *Gummi-Ztg.*, **43**, 22 (1928); *Chem. Abs.*, **23**, 306 (1929).

³ For x-ray data on crystals in stretched rubber, see Clark, G. L., *Ind. Eng. Chem.*, **18**, 1131 (1926).

⁴ For the Raman spectrum of rubber, see Gehman, S. D., *J. Am. Chem. Soc.*, **57**, 1382 (1935).

⁵ Kirchhof, F., *Kautschuk*, **4**, 254 (1928); *Chem. Abs.*, **23**, 1525 (1929).

⁶ Kirchhof, F., *Kautschuk*, **28**, 1927; *Chem. Abs.*, **21**, 1377 (1927).

⁷ Porritt, B. D., *India Rubber J.*, **60**, 1159 (1920); *Chem. Abs.*, **15**, 1230 (1921).

⁸ Gallay, W., *Canadian J. Res.*, **7**, 671 (1932); *Chem. Abs.*, **27**, 1561 (1933). See, however, Dogadkin, B., and Lavrenenko, M., *Kautschuk*, **9**, 97 (1933); *Chem. Abs.*, **27**, 4953 (1933).

⁹ Kambara, S., *J. Soc. Chem. Ind. Japan*, **39**, 138 (1936); *Chem. Abs.*, **30**, 6298 (1936).

¹⁰ Garner, T. L., *Trans. Inst. Rubber Ind.*, **4**, 413 (1929); *Brit. Chem. Abs.*, **B**, 445 (1929).

rubber stands in no simple relation to their effects on actual oxidation. By favoring the formation of an insoluble polymer on the surface of exposed rubber, anti-oxidants may, indeed, accelerate the loss of surface tackiness.

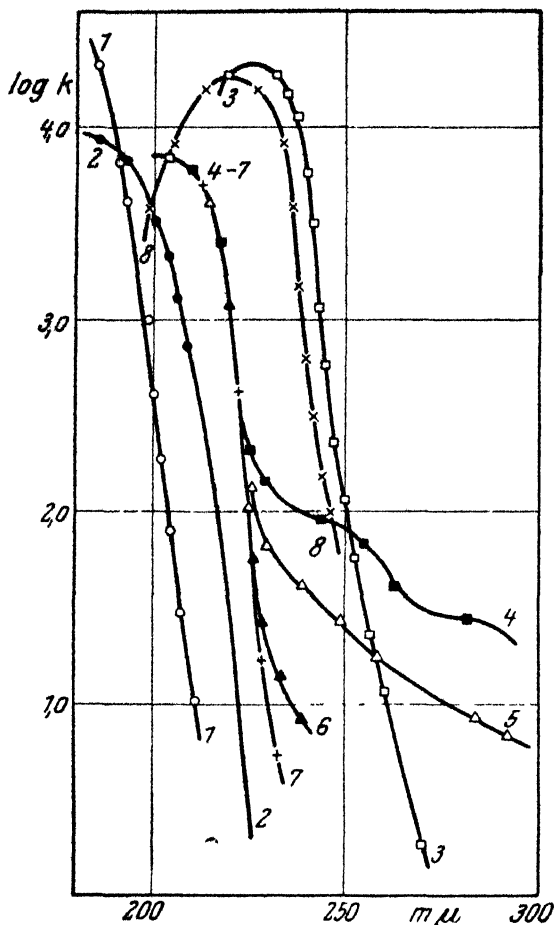


FIGURE 127.

Absorption of Latex, Sol-Rubber and Related Compounds (Scheibe and Pummerer, *Berichte der deutschen Chemischen Gesellschaft*).

1. Diallyl
2. Trimethylethylene
3. Dimethylbutadiene
4. Latex purified with NaOH and coagulated
5. Latex, uncoagulated
6. Latex, purified with NaOH
7. Sol rubber
8. Isoprene

Mojen¹¹ found that no change in the viscosity of ordinary rubber solutions containing monochloroacetic acid occurs in light when oxygen is rigorously excluded. The same was true also of balata solutions containing acetic acid or its chlorine substitution products. But with oxygen present, the rubber sols changed to an insoluble product even in darkness. The protective power of the natural anti-oxidants, which are probably basic, is destroyed when they are combined with acids. A benzene solution of purified gutta-percha irradiated in an atmosphere of hydrogen gave on evaporation a white, unctuous, fragile product which melted to a limpid oil at 90°C. On cooling, the latter gave a tough product like the original gutta-percha, so that heating was assumed to have destroyed the crystalline struc-

¹¹ Mojen, H. P., *Kautschuk*, 13, 39 (1937); *Chem. Abs.*, 31, 5214 (1937).

ture. The melting point of the microcrystals of the irradiated material was believed to be lower than that of the crystals which are obtained in films formed by evaporation of nonirradiated solutions. The product left after the evaporation of the benzene from an irradiated solution redissolved to a clear solution in benzene, if the irradiation is conducted in hydrogen; but irradiation of a film with air present gives a product which is partly insoluble. Such effects are not observed in the case of rubber. The different behavior of gutta-percha is ascribed to its higher state of polymerization.

No change in the unsaturation of a 1-per cent solution of pale crepe rubber can be detected by a modified Wijs method after irradiation under carbon dioxide in a quartz flask for 28 to 45 hours by a quartz mercury-vapor arc.¹²

The ultraviolet radiations present in sunlight tend to polymerize rubber, isoprene and styrene, especially in the presence of sensitizers (compare the cinnamic acids, Chapter 25).¹³ Ether solutions of rubber under nitrogen in sealed tubes generally gelatinize when exposed to sunlight, but the length of time required, sometimes weeks, varies so greatly that this is not a practicable method of bringing about gelation. The light rubber obtained by evaporating the ether gel is entirely insoluble in ether if the illumination has been sufficiently prolonged. On milling rolls, it gradually becomes ether-soluble again, but it differs from gel rubber in that the addition of diethylamine, piperidine, etc. does not make it ether-soluble. Its iodine number is 94 to 98 per cent of that of the original sol rubber. Apparently the chemical effect of the irradiation is a polymerization involving only from 2 to 6 per cent of the double bonds. The gelation can be regulated and reproduced at will by the use of various sensitizers containing a carbonyl group. With eosin, gelation can be demonstrated in about ten minutes in quartz under a mercury arc, and even 0.2 per cent solutions of rubber in carbon tetrachloride can be made to gel. It is the longer wave lengths between 2800 and 3150A which are believed effective. Methylene blue and malachite green offered no advantages over eosin. Diphenylketone (3150 to 4000A) and benzanthrone (3150 to 4200A) are also effective. Benzaldehyde also produces gelation, but with it and with acetaldehyde the conditions do not seem as simple as with the ketones. Methylbenzyl oxide proved to be moderately effective, but aliphatic esters and such colored hydrocarbons as perylene had no action. The same sensitizers also bring about the gelation of liquid isoprene and isoprene emulsions in soap solutions in glass. The resulting isoprene rubbers give iodine numbers of 94 to 99 per cent of the theoretical, but with evolution of considerable quantities of hydrogen iodide.

Liquid styrene is readily polymerized to solid styrene resin in glass in the presence of sensitizers in several days of exposure to a 200-watt lamp at room temperature. In the presence of diphenyl ketone or benzanthrone at 60-70°C. and with a 500-watt lamp, the change is complete in a few hours. The reaction proceeds two to three times as rapidly under cylinder nitrogen containing some oxygen as it does under pure nitrogen. Since it is oxygen in the gas phase that is effective, it may be assumed that gelation begins at the gas-liquid interface. Such antioxidants as hydroquinone inhibit the reaction. The presence of "active oxygen" during the irradiation of diphenyl ketone, phenylmethyl ketone and even of diethyl ketone was shown by means of a benzidine-sodium chloride solution. Iron compounds (ferric chloride, ferric acetylacetonate, iron pentacarbonyl) do not accelerate the photogelation of rubber solutions. Kirchhof¹⁴ also noted that when a

¹² Fisher, H. L., and Gray, A. E., *Ind. Eng. Chem.*, **18**, 414 (1926).

¹³ Pummerer, R., and Kehlen, H., *Ber.*, **66B**, 1107 (1933); *Chem. Abs.*, **27**, 6018 (1933).

¹⁴ Kirchhof, F., *Kautschuk*, **28**, (1927); *Chem. Abs.*, **21**, 1377 (1927).

benzene solution of phosphorus is added to a rubber solution before exposure, irradiation produces a gel similar to that produced with dilute sulfur chloride. This gel is formed even in rubber solutions which have previously been depolymerized by light. If rubber-phosphorus solution which has been exposed to light but not gelatinized is evaporated and extracted with acetone, the resulting rubber is similar in physical properties to rubber vulcanized with sulfur chloride. Similarly treated samples in which no phosphorus had been added gave only a weak, tacky product. There is no change apparent in phosphorus-containing benzene solutions of rubber exposed in carbon dioxide to daylight at 70-75°C. Without rubber present, benzene solutions of yellow phosphorus deposit red phosphorus on exposure to ultraviolet light or to sunlight, but rubber has a protective action so that in its presence this reaction does not occur. The phosphorus photovulcanization occurring in rubber solutions in ultraviolet light resembles sulfur vulcanization in that gel formation is greatly accelerated by zinc xanthate.

In latex, polymerization by quinone is readily aided by irradiation.¹⁵ At 90°C., air causes depolymerization, even in light. When portions of quinone and latex were irradiated separately and mixed in darkness, no enhanced polymerization resulted. It also does not result from the irradiation of latex alone. The photochemical polymerization is not inhibited by an excess of hydroquinone, but it is greatly reduced by an excess of a dark brown oxidation product of quinone, which may compete in absorbing the effective light. When a solution of rubber in benzene containing quinone is irradiated in the presence of air, there is marked depolymerization at room temperature, but irradiation at -80°C. leads to enhanced polymerization.

The addition of an inorganic cobalt salt or of cobalt resinate to a benzene solution of rubber causes rapid depolymerization, which is accelerated by air and light.¹⁶ The effects of many antioxidants and accelerators upon the development of tackiness in rubber when exposed to a General Electric S-1 lamp have been determined by Blake and Bruce.¹⁷

Irradiation of chloroprene by the 2537A line leads, after a long induction period, to a polymerization in the condensed phase. A dark polymerization subsequently ensues.¹⁸ Butadiene shows little tendency toward photopolymerization and the quantum yield in the mercury-sensitized reaction is only unity. This compound admixed with methyl methacrylate inhibits the photopolymerization of the latter, which in the absence of this inhibitor has a quantum yield of about one hundred.

No indication of a *cis-trans* transformation by ultraviolet could be found by Meyer and Ferri,¹⁹ although they state that light effects a kind of "vulcanization" by irregular polymerization. When solutions of 1 g. and 2.5 g. of coagulated latex in 100 cc. of cyclohexane were irradiated in a quartz flask in oxygen for ten hours at 5 cm. from a 300-watt quartz mercury arc, elastic gels insoluble in solvents were formed. These were similar to products obtainable by the addition of small amounts of sulfur chloride. Dry gels formed in the absence of oxygen had the mechanical properties of a feebly vulcanized rubber. It is believed that in such gels, the original rubber hydrocarbon chains are oriented in a three-dimensional

¹⁵ Spence, D., and Ferry, J. D., *J. Am. Chem. Soc.*, **59**, 1648 (1937).

¹⁶ Krauz, C., and Franta, I., *Rubber Tech. Conf., London, Preprint No. 13* (May, 1938); *Chem. Abs.*, **32**, 8169 (1938).

¹⁷ Blake, J. T., and Bruce, P. L., *Rubber Tech. Conf., London, Preprint No. 21* (May, 1938); *Chem. Abs.*, **32**, 8833 (1938).

¹⁸ Bolland, J. L., and Melville, H. W., *Rubber Tech. Conf., London, Preprint No. 90*, May, 1938; *Chem. Abs.*, **32**, 8396 (1938).

¹⁹ Meyer, K. H., and Ferri, C., *Helv. Chim. Acta*, **19**, 694 (1936); *Chem. Abs.*, **30**, 6601 (1936); *Rubber Chem. Tech.*, **9**, 570 (1936).

network through the establishment of valence bonds transversely and between the double bonds.

It has been observed that gasoline rubber cements exposed to sunlight in glass in most cases became solvent-thin, although in a few cases gels formed.²⁰ Carbon tetrachloride cements all formed rigid gels. The behavior of the latter is ascribed to a curing by ultraviolet light and by chlorine resulting from decomposition of the solvent. Similar results were obtained at a slower rate in diffused light. Protection of the gasoline cements by red filters greatly prolonged the time required for them to thin. The higher the rubber content of a cement, the smaller is the change in its viscosity.

VULCANIZATION

Victor Henri is credited by Helbronner with having used ultraviolet rays as early as 1909-10 for the vulcanization of films made from solutions of rubber. Rubber solutions vulcanized by ultraviolet are stated by Helbronner²¹ to be insoluble in the original solvent after they have been dried. Bernstein²² proposed vulcanizing rubber solutions containing sulfur by exposing them to the action of ultraviolet rays produced by a quartz mercury-vapor lamp, the solutions being spread on a moving metallic ribbon. A solution of rubber in benzene containing 6 per cent of rubber, and sulfur equal to 10 per cent of the rubber, when exposed in a film 0.5 mm. thick required forty to fifty seconds for vulcanization. Ordinary or high temperatures, pressure or vacuum, air or inert gas atmospheres, may be used. Bernstein²³ evaporated a xylene solution of Hevea plantation rubber with 6 per cent of sulfur to a thin film on a transparent quartz plate and covered it with another quartz plate. This was exposed on both sides for forty minutes at a distance of 15 cm. to the rays from a Heraeus lamp of three amperes and 110 volts. The film then possessed the properties of vulcanized rubber and contained 2.56 per cent of combined sulfur. Other experiments showed that the percentage of combined sulfur increased with the time of exposure to the rays. The deterioration of vulcanized rubber on exposure to ultraviolet rays, observed by Henri, is considered to be chiefly due to "after-vulcanization." Stern²⁴ states that the vulcanization is accompanied by some depolymerization. Ostromuiskenski²⁵ believed that, in the absence of air, the rays activate sulfur by converting it into thiozone. The vulcanization is then affected partly by the latter and partly by the ozone formed simultaneously.²⁶

According to Pohle,²⁷ irradiation of a supersaturated solution of sulfur in rubber, prepared by heating, results in separation of the sulfur. The effect, which is due to the violet and blue rays, can be followed ultramicroscopically by a quartz ultra-condenser. The number of particles depends on the intensity of the light and on the time of exposure. Long exposures or high intensities give dense, fine, blue

²⁰ Novotny, C. K., *Ind. Eng. Chem.*, **26**, 170 (1934).

²¹ Helbronner, A., *India Rubber World*, 130 (1914); note also *Compt. rend.*, **138**, 1343 (1914); *Chem. Zentralbl.* 326, (1914); *Kolloid Z.*, **4**, (1913); French P. 460,780, July 26, 1913.

²² Bernstein, G., British P. 17,195, July 26, 1913; U. S. P. 1,240,116, Sept. 11, 1917.

²³ Bernstein, G., *J. Frank. Inst.*, **345**, 1913. Note also Helbronner, A., and Bernstein, G., *Rubber Ind.*, 156 (1914); *Caoutchouc et Gutta-Percha*, **12**, 8720 (1915). Green, H., *Ind. Eng. Chem.*, **17**, 802 (1925) has used the ultraviolet microscope in connection with a study of vulcanized latex globules; see also Lucas, F. F., [*Ind. Eng. Chem.*, **30**, 146 (1938)] for observations on untreated latex. Note also Gray, G. W., *Technology Rev.*, **40**, 172, 188, 190, 192 (1938).

²⁴ Stern, E., *Chem. Ztg.*, Rep. 422 (1913).

²⁵ Ostromuiskenski, I. I., *J. Russian Phys. Chem. Soc.*, **47**, 1892-1898 (1915); *J. Soc. Chem. Ind.*, 370 (1916).

²⁶ Meyerinhg, D. J., and Wijnand, P. C., British P. 208,167, Dec. 24, 1924; *Chem. Abs.*, **18**, 1589 (1924).

²⁷ Pohle, H., *Naturwiss.*, **15**, 162 (1927); *Chem. Abs.*, **21**, 1904 (1927).

dispersed fogs and short exposures give a smaller number of more rapidly growing droplets. The smallest effect, one to five particles, resulted from an exposure of .01 second to a 5-ampere lamp. The sulfur particles are apparently liquid. The sensitivity to light is diminished by the presence of substances which absorb blue or violet rays. The sulfur then appears only at the surface. This effect of light is also inhibited by even the slightest vulcanization of the rubber, and it can therefore serve as an indication of the vulcanization process. The effect is observed as far below the surface as the light penetrates.

During the vulcanization of rubber by phosphorus in ultraviolet light, there appear after prolonged illumination of the optically empty rubber-phosphorus-benzene system, glistening phosphorus particles 0.5 to 2.1μ in diameter.²⁸ This formation of nuclei by ultraviolet has its analogy in the transformation of yellow to red phosphorus. A similar turbidity appeared on ultraviolet illumination of a carbon disulfide solution of sulfur containing piperidine pentamethylenedithiocarbamate.

Kirchhof also states²⁹ that vulcanization of rubber in ultraviolet light by trinitrobenzene or picric acid, especially the former, yields results comparable with those of cold vulcanization. These products, like ordinary vulcanizates, show strong absorption of ultraviolet radiations.

In producing lustrous spread rubberized material, Ditmar³⁰ spreads the material in the usual way with a benzene solution of a mixture containing crepe rubber 100 parts, colloidal sulfur 3.5 parts, tetramethylthiuramdisulfide 2 parts, Sulzin (*i.e.*, zinc sulfate-5 NH_3), 7 parts, anhydrous sodium thiosulfate 2 parts, selenium red 1.8 parts and titanium oxide 2 parts. It is then led directly under a battery of quartz mercury lamps, the exposure being for five minutes at a distance of 8 cm. Complete vulcanization results with the production of a non-tacky rubber surface of high lustre.

It was necessary to carry out the process of Bernstein³¹ in an inert gas or *in vacuo* to prevent oxidation by the ozone. But when tetramethylthiuramdisulfide is used as an accelerator to minimize the curing time and exposure, and with selenium red as a protective agent, it is possible to cure the spread material in air. Ditmar³² also showed that ultraviolet radiation has itself an oxidizing action on accelerated rubber mixtures which predominates over the vulcanization. Therefore, from a practical point of view, satisfactory vulcanization is possible only when a red or yellow protective pigment, such as selenium red, is added. With an activator like zinc oxide present in an accelerated mixture, ultraviolet radiation brings about vulcanization in a short time. The duration of the exposure must be carefully controlled to prevent oxidation, under-curing or over-curing. Ultraviolet radiation has the most favorable effect on rubber mixtures accelerated by tetramethylthiuramdisulfide and containing an activator. Surface vulcanization is complete in four and a half minutes without oxidation even in the absence of a protective red pigment.

Surface vulcanization by light is regarded as a true vulcanization process since it has been proved that sulfur must be present. It is believed that the sulfur is activated by the radiation and then enters into reaction with the rubber.³³ Ditmar and

²⁸ Kirchhof, F., *Kautschuk*, 184 (1927); *Chem. Abs.*, 21, 2819 (1927).

²⁹ Kirchhof, F., *Gummi-Ztg.*, 44, 252 (1929); *Chem. Abs.*, 24, 750 (1930).

³⁰ Ditmar, R., *Gummi-Ztg.*, 43, 1172 (1929); *Brit. Chem. Abs.*, B, 294 (1929); *Chem. Abs.*, 23, 2602 (1929).

³¹ Bernstein, G., *German P.* 262,708, 1912.

³² Ditmar, R., *Gummi-Ztg.*, 43, 1172, 2325 (1929); *Chem. Abs.*, 23, 2602, 4374 (1929).

³³ Ditmar, R., and Grünfeld, O., *Gummi-Ztg.*, 43, 2801, 2859 (1929); *Chem. Abs.*, 23, 5612 (1929).

Grünfeld find that, when about 3 per cent of sulfur is present, the addition of organic accelerators can be completely dispensed with. Indeed, many organic accelerators may have an unfavorable action. In most cases, Vulkan colors give excellent shades of color under these conditions, and in combination with other organic and inorganic colors such as selenium red or methylene blue, all kinds of colors and tones can be obtained. In general, ultraviolet vulcanization can be effected in four to eight minutes at 20-90°C., depending upon the support on which the sample rests, the shortest times being obtained on glass. This influence of the support apparently depends upon its heat conductivity and heat capacity, for the higher the temperature prevailing during the process, the more rapid its rate.

Formulas of blue, green, orange, red and brown rubber mixtures which will cure in seven minutes at a distance of ten cm. from the ultraviolet source are given by Ditmar and Preusze.⁸⁴

In patents of the Goodyear Tyre and Rubber Co.⁸⁵ the appearance and dirt-resisting qualities of vulcanized rubber are claimed to be improved by exposure to ultraviolet radiation.

On the assumption that the increase in the electrical conductivity of hard rubber on exposure to light and air is a result of the formation of a surface film containing acid, Fry and Porritt⁸⁶ carried on experiments to ascertain the mechanism of its formation. It was found that hydrogen sulfide is evolved, the rate of evolution being the greatest in direct sunlight. This may, however, be the result of thermal rather than light action. This evolution of hydrogen sulfide results from a decomposition of the rubber-sulfur compound and occurs in the absence of free sulfur, resins, oxygen and water vapor. Its rate increases with a rise of temperature.

Ultraviolet vulcanization has been employed in the production of surface designs on rubber.³⁷ A surface of a rubber sheet to be etched is vulcanized by the action of ultraviolet rays or by sulfur chloride, a design is formed on the surface and an etch-resist may be incorporated with the inked parts. A mixture of nitric acid and potassium dichromate is used for etching and the etched sheet is washed with acetone or alcoholic soda solution. Silica and fat-containing fillings should not be present in the rubber.

Rimpel and Hermann³⁸ state that when strong reducing agents, such as a light-sensitive silver bromide gelatin, are mixed into the rubber, it is possible to form designs or pictures directly by exposure to the light. They do not agree with the suggestion of Defries and Naunton that a discoloration on irradiation is the result of an over-vulcanization produced by light on the surface. When four mixtures, each containing rubber, lithopone and zinc oxide, and the first also sulfur; the second, accelerator; the third, sulfur and accelerator, and the fourth, no addition, were exposed to sunlight for thirty minutes, the first and fourth mixtures remained unchanged, but the second and third became discolored to an equal extent. This indicates that the discoloration depends only on the accelerator and has no direct relation to the state of vulcanization. The accelerator thus behaves like a reducing agent.

⁸⁴ Ditmar, R., and Preusze, K. H., *Caoutchouc & gutta-percha*, 26, 14,762 (1929); *Gummi-Ztg.*, 43, 2749 (1929); *Brit. Chem. Abs.*, B, 863 (1929); *Chem. Abs.*, 24, 749 (1930).

⁸⁵ British P. 404,120, Nov. 10, 1932, to Goodyear Tyre and Rubber Co; French P. 749,642, July 27, 1933; *Chem. Abs.*, 28, 685 (1934).

⁸⁶ Fry, J. D., and Porritt, B. D., *India Rubber J.*, 78, 307, 309 (1929); *Chem. Abs.*, 23, 5613 (1929).

³⁷ British P. 241,542, Oct. 14, 1924, to Soc. d'Exploitation des Procédés d'Impression Sardou; *Chem. Abs.*, 20, 3590 (1926).

³⁸ Rimpel, H., and Hermann, P., *Gummi-Ztg.*, 43, 2270 (1929); *Chem. Abs.*, 23, 4370 (1929); German P. 448,972; see also Defries, R., and Naunton, W., *Trans. Inst. Rubber Industry*, 4, 298 (1928); *Chem. Abs.*, 23, 2068 (1929).

Fluorescence of Accelerators. Various accelerators are readily distinguished by their characteristic fluorescence colors in filtered ultraviolet light. When present alone in pale crêpe, some of them may be detected by this method.³⁹ Even when some other ingredients, such as sulfur, zinc oxide, magnesia, lead oxide, etc., are present, it is possible, in some cases, to distinguish a characteristic appearance. However, with several ingredients present, the fluorescent effect varies with the different combinations, and only when the composition of the mixture is known can the method be employed for the detection of accelerators. Characteristic colors are also obtained after vulcanization, although they are different from those observed in the same mixtures prior to vulcanization.⁴⁰ The approximate quantity may be judged within ± 5 per cent if the fluorescent light from filtered ultraviolet is passed through an actinometer containing a triphenylmethane dye. Dittmar⁴¹ has listed the fluorescence colors of a number of accelerators. The change of fluorescent color on prolonged irradiation is also of significance.

Nagle⁴² employed this method for the study of the pigments used in the industry. In the examination of eight grades of zinc oxide mixed with glycerol, one appeared light green, one light gray-green, one light green-gray, two orange-buff, one bright apple-green, one pale dull violet and one deep violet. After having been kept ten minutes at a white heat, all were green. The same distinctive shades were visible in rubber mixtures when a small proportion was used in vulcanizing the rubber with sulfur, accelerator and lithopone. Even when the rubber mixtures were made dark gray by the addition of carbon black, the individual samples containing zinc oxide could still be distinguished. In lithopones, the range of colors was not so great, the samples appearing deep violet, pale violet, brown or almost white. An examination of rubber imperfectly mixed with zinc oxide and lithopone revealed the characteristic colors of the two pigments and indicated the possibility of determining the distribution of powders in rubber mixtures. The lithopones which appeared deep violet were the most nearly sunproof. Those which appeared white darkened the most rapidly. In filtered ultraviolet light, however, the latter were resistant, indicating the radiation responsible for the darkening to be of wave-length shorter than that transmitted by the filter used (3300-3900 Å). Mineral oils and Vaseline were fluorescent and phosphorescent, coal-tar showed a faint, yellow-brown fluorescence and sulfur assumed a bronze color. In the form of bloom, it can be readily distinguished by this method. Addition of 1 per cent of coal tar to a black rubber mixture changed its appearance in filtered ultraviolet light from very dark violet to gray-blue. Various tire sections appeared violet, brown-violet, blue, green, yellow and brown-red, since various other added substances exhibited characteristic fluorescences.⁴³

Kirchhof⁴⁴ reported similar observations, but differed from Nagle in believing the purest grade of zinc oxide to be sulfur-yellow. Since zinc sulfide gives a bright orange color, the fluorescence of lithopone varies with its zinc sulfide content. Among aliphatic substances, vegetable and animal oils, fats and waxes and paraffin hydrocarbons show characteristic colors. Phenols and aromatic acids exhibit particularly bright colors, the intensity apparently increasing with the complexity of the ring. Nitro-groups weaken the fluorescence. Dyes, accelerators and antioxidants are also distinguished by characteristic colors in this manner. The differences in the appearance of various rubbers in filtered ultraviolet depend chiefly upon material which can be extracted by acetone. It was suggested that the method might be of value in following the natural or artificial aging of rubber mixtures by oxidation.

Dittmar⁴⁵ employed the method particularly for the study of accelerators. The color of mercaptobenzothiazole, for example, varied with the manufacturer. Kojima and Nagai⁴⁶ reported observations on 41 such substances. Morris⁴⁷ considered especially the substances important in American manufacture. The personal element plays a large part in the recording of the colors, so that it is necessary to have standard samples available for comparison. Morris believed the color variation in samples of zinc oxide

³⁹ Dittmar, R., and Dietsch, W., *Chem. Ztg.* **52**, 388 (1928); *Gummi-Ztg.*, **42**, 1415 (1928).

⁴⁰ M. L. P., *Rev. gen. caoutchouc*, **6**, No. 53, 9 (1929); *Chem. Abs.*, **23**, 5612 (1929).

⁴¹ Dittmar, R., *Chem. Ztg.* **52**, 730 (1928); see also Garner, T. L., [*India Rubber J.*, **77**, 31 (1929); *Chem. Abs.*, **23**, 1772 (1929)] for the identification of antioxidants by this method.

⁴² Nagle, P. G., *Trans. Inst. Rubber Industry*, **3**, 304 (1927); *Chem. Abs.*, **22**, 1251 (1928).

⁴³ Nagle, P. G., *Rubber Chem. & Tech.*, **1**, 284 (1928).

⁴⁴ Kirchhof, F., *Kautschuk*, **4**, 24 (1928); *India Rubber J.*, **75**, 791 (1928); *Chem. Abs.*, **22**, 2291 (1928).

⁴⁵ Dittmar, R., *Caoutchouc & gutta-percha*, **28**, 15,685 (1931); *Chem. Abs.*, **25**, 6017 (1931).

⁴⁶ Kojima, K., and Nagai, I., *J. Rubber Soc. Japan*, **2**, 260 (1930); *Chem. Abs.*, **25**, 3871 (1931).

⁴⁷ Morris, V. N., *Ind. Eng. Chem.*, **26**, 107 (1934).

to be related to a certain extent to the particle size. Well-vulcanized rubber shows a yellow fluorescent color of fairly strong intensity, but decidedly undercured rubber fluoresces only slightly. Rubber loses its fluorescence almost completely after an hour in direct sunlight. For this change, oxygen is not essential. In general, no definite relation is apparent between the optimum physical properties of rubber and the intensity of its fluorescence.⁴⁸

Fluorescence tests may also be employed in judging the progress and uniformity of vulcanization. The light emitted by mixtures containing three to eight per cent of sulfur increases with the state of vulcanization. The fluorescence changes are accelerated by zinc oxide.⁴⁹ With ten per cent or more of sulfur, when semi-ebonites are formed, the fluorescence becomes brown-red and less intense. Undercured rubber mixtures, in general, show relatively weak fluorescence and overcured ones a strong fluorescence, greenish for rubber and sulfur mixtures and yellowish-green for accelerated mixtures. Excessive overcuring may make the fluorescence yellow. The fluorescence of Neoprene also increases during vulcanization without sulfur but less markedly than in the case of rubber. Oberto⁵⁰ has also described the changes in fluorescence of vulcanized rubber during aging, natural or artificial. In the initial stages (one minute in sunlight), it changes to violet, even before an alteration of mechanical properties can be noted. Later it becomes more intense, finally changing to ochre or red, depending upon the sulfur content, at complete deterioration (ten hours of exposure). The presence of other substances may complicate the fluorescence effects.

LIGHT AND THE OXIDATION OF RUBBER

In reviewing this topic, Shepard, Krall and Morris⁵¹ state that as early as 1865, Spiller⁵² proved that oxygen functions in the change undergone by strained rubber in light. Burghardt⁵³ believed that light alone would injure perfectly good normal vulcanized rubber only when acting in conjunction with other destructive agents. Fickendey⁵⁴ showed that samples exposed to direct sunlight in sealed tubes in hydrogen, nitrogen and carbon dioxide remained unchanged for weeks, although rubber exposed under oxygen became sticky. Ahrens,⁵⁵ Peachy and Leon,⁵⁶ and Henri⁵⁷ considered sun-checking or sun-cracking an oxidation process aided by both light and heat.

Asano⁵⁸ observed that when rubber is exposed to ultraviolet light under carbon dioxide, nitrogen or hydrogen, it is converted into two products of much the same composition. One was a white, opaque, brittle, polymerized substance, insoluble in benzene. The other was a depolymerized, tacky product of reduced viscosity. Similar behavior was observed during exposures in air. Asano believed that radiations longer than 3100Å had no significant effect, and that these physical and chemical changes were most rapid and profound under the influence of wave-lengths between 2250 and 2000Å. Some dyes, however, sensitize rubber to longer wave-lengths. These changes were largely independent of oxidation, which occurred to a considerable extent only in sunlight, and caused tackiness, followed by brittleness. The ultimate products were insoluble in boiling benzene, chloroform, alcohol or acetone, and contained 14.6 per cent of oxygen. The action

⁴⁸ For a general review of fluorescence tests for rubber, see Hauser, E. A., and Le Beau, S., *Kautschuk*, **10**, 113 (1934); Krah, M., *Kautschuk*, **159**, 180 (1927).

⁴⁹ Oberto, *Gomma*, **1**, 157 (1937); *Chem. Abs.*, **32**, 3198 (1938).

⁵⁰ Oberto, S., *Rubber Tech. Conf. London, Preprint No. 75*, May, 1938; *Chem. Abs.*, **32**, 8212 (1938).

⁵¹ Shepard, N. A., Krall, S., and Morris, H. L., *Ind. Eng. Chem.*, **18**, 615 (1926).

⁵² Spiller, J., *J. Chem. Soc.*, **18**, 44 (1865).

⁵³ Burghardt, C. A., *J. Soc. Chem. Ind.*, **2**, 119 (1883).

⁵⁴ Fickendey, E., *Kolloid Z.*, **9**, 81 (1911).

⁵⁵ Ahrens, F., *Kunststoffe*, **3**, 478.

⁵⁶ Peachy, S. J., and Leon, M., *J. Soc. Chem. Ind.*, **37**, 56T (1918).

⁵⁷ Henri, V., *Caoutchouc & Gutta-percha*, **7**, 4372 (1910).

⁵⁸ Asano, K., *India-Rubber J.*, **70**, 307, 347, 389, 395 (1925); *Chem. Abs.*, **19**, 3616 (1925).

involved an initial depolymerization, with subsequent accelerated oxidation of the depolymerized product. The oxidation was induced by wave-lengths shorter than 5000A, and the depolymerization by longer wave-lengths. Elimination of the infrared rays by a water filter did not alter the action of sunlight. The intensity of light governed the rapidity of the changes. Asano also alluded to the deleterious action of ozone.

Williams⁵⁹ definitely showed that 5 grams of emery-wheel buffings of a pure gum inner tube absorb oxygen more rapidly in sunlight (0.93 cc. per hour) than in darkness (0.13 cc. per hour). Light had, however, little effect upon unstrained strips of the same rubber. The success in the case of the buffings was due to the fact that the fresh surfaces clung together in such a manner as to keep the small particles in a strained condition.

It was claimed by de Jong⁶⁰ that in a quartz vessel exposed to sunlight in the Dutch East Indies, a benzene solution of crepe rubber absorbed a considerable volume of air. In later experiments with less intense sunlight in Holland, the same process occurred behind glass, but less rapidly. In eight days, 25 cc. of air were completely absorbed by 325 cc. of solution. de Jong claimed also that after six days of exposure in sealed tubes under nitrogen, a 1.05-per cent solution of rubber in benzene absorbed 2.5 per cent of nitrogen and that the absorption of this gas by the hydrocarbon from balata gutta-percha after purification with petroleum ether also occurs. However, nitrogen absorption by rubber has been denied by Howard and Hilbert.⁶¹ Dogadkin and Panchenkov⁶² observed that on irradiation of rubber solutions in nitrogen, the interfacial tension against water did not change. When irradiated in air, it was lowered and reached a constant value in two hours.

Bondy and Lauer⁶³ found, in agreement with Staudinger and Leupold, that rubber solutions do not autoxidize in darkness. In light, the solutions decomposed in the same manner whether or not the natural antioxidant was present. There was no decomposition when the exposures were made in nitrogen; only in light and air were positive results attained.

Williams⁵⁹ also showed that the exposure of strips of a vulcanized gray side-wall stock stretched to an elongation of 5 per cent, and exposed in air or oxygen (but not in evacuated tubes) to July sunlight daily for two weeks appeared slightly wrinkled. Upon releasing the strain, the wrinkled appearance became pronounced, showing that a non-elastic skin had formed on the surface. The weight had increased slightly. The skin had a glazed appearance, was almost inelastic but not brittle and was soluble in alcohol. The surface beneath appeared unchanged and no decrease in tensile strength could be observed. Light-colored rubber will form, in some cases, a pronounced skin in two days of exposure to the sun.

Tests by Williams with various colored filters indicated that the short wave-lengths of visible light from a tungsten lamp were most effective in producing surface oxidation. White light produced the heaviest skin. The amount of oxidation was directly dependent upon the intensity of the light. A mercury lamp placed ten inches from the strip elongated at about 10 per cent produced a pronounced surface oxidation in three hours. If, however, the mercury lamp is placed two to three feet from the strip no skin formed. Instead, after one or two hours, small cracks began to appear in the surface of the rubber. These continued to

⁵⁹ Williams, I., *Ind. Eng. Chem.*, **18**, 367 (1926).

⁶⁰ de Jong, A. W. K., *Rec. trav. chim.*, **51**, 133 (1932).

⁶¹ Howard, L. B., and Hilbert, G. E., *J. Am. Chem. Soc.*, **59**, 214 (1937).

⁶² Dogadkin, B., and Panchenkov, G., *Kolloid-Z.*, **65**, 350 (1933); *Chem. Abs.*, **28**, 1890 (1934).

⁶³ Bondy, H. F., and Lauer, G. G., *Ber.*, **66B**, 1611 (1933).

increase in size and number, but the surface between the cracks remained unchanged except on prolonged exposure. This type of oxidation, due to it was believed to ozone, is characterized by extreme rapidity and by a negligible increase in weight.⁶⁴ In direct ozonizing tests, it was necessary to reduce the concentration of ozone to about one part in 50,000 of air in order to reduce the speed of cracking to a point at which observations could be accurately made. Surface oxidation appears to be to some extent an efficient protection against even a relatively high concentration of ozone, since this cracking was not observed in samples which had been exposed ten inches from the lamp. Checking can be retarded by catalyzing the surface oxidation by means of copper salts.⁶⁵ Compounds containing zinc oxide are more easily protected than pure gum type compounds.

The basic components of the acetone-soluble material from rubber account for the antioxidant effect of both rubber and balata, according to Bondy and Lauer.⁶⁶ The acids, amino-acids and bases of the serum and phenols have a slight antioxidant effect. The neutral components and acid amides are inactive in this respect. Heating rubber or balata resin at 120°C. increases its protective action against ultraviolet light. Those rubber solutions which had the deepest brown color had the least tendency to autoxidize. Further experiments showed that a dye present in the rubber retards autoxidation by absorbing the active radiations. Tests of known dyes proved that some have a marked protective action by internal filtering, but others were only slightly protective.

Bondy,⁶⁷ irradiated purified balata in the solid state in air with sunlight and with ultraviolet light, determining the extent of autoxidation by measuring the viscosity of Tetralin solutions of a concentration corresponding to 0.2 molecule of isoprene, before and after irradiation, *i.e.*, by the general method of Staudinger. Rubrene and dehydrorubrene had almost no effect on the reaction. Bidiphenylene-ethylene and β -naphthoquinone were active antioxidants, but anthraquinone showed strong proöxygenic influence. Paraquinone had no effect and acenaphthenequinone almost none. Aldol- α -naphthylamine as well as an acetone extract of rubber had weak, and phenanthrenequinone or α -naphthoquinone strong polymerizing influence. The most highly colored compounds were the strongest antioxidants. Aldol- α -naphthylamine reduced slightly the polymerizing action of α -naphthoquinone.

When balata in solution was irradiated, rubrene and dehydrorubrene were distinct proöxygens, whereas bidiphenylene-ethylene and an acetone extract of rubber were without influence. Passage of the light through a toluene filter had no influence on its oxidizing action on balata or acetone-extracted rubber exposed to the air. All substances which acted as antioxidants when added to the rubber showed the same property when employed as external filters. Azobenzene and α -benzeneazo- β -naphthylamine also prevented autoxidation and α -naphthoquinone, phenanthrenequinone and alizarine retarded it greatly when their solutions were used as filters. A colored substance which absorbs active radiations inhibits autoxidation only if it is soluble in balata or acetone-extracted rubber. The antioxygenic power of an acetone extract of rubber depends in part upon its brown color, for even in very low concentrations, *e.g.*, 0.1 per cent in toluene as a light filter, it still retarded autoxidation. This does not mean, however, that the antioxygenic power depends only on the colored components. By means of filters, the spectral region

⁶⁴ See also van Rossem, A., and Talen, H. W., *Kautschuk*, 7, 79, 115 (1931); *Chem. Abs.*, 25, 5795 (1931).

⁶⁵ This could not be confirmed by van Rossem, A., and Talen, H. W., *Kautschuk*, 7, 79, 115 (1931); *Chem. Abs.*, 25, 5795-6 (1931).

⁶⁶ Bondy, H. F., and Lauer, G. G., *Ber.*, 66B, 1611 (1933).

⁶⁷ Bondy, H. F., *Rev. gen. caoutchouc*, 11, No. 1, 6, 9 (1934); *Chem. Abs.*, 29, 4207 (1935).

which is active in autoxidation in sunlight was found to lie between 3000 and 4800Å. In this ultraviolet region, the activity was apparently uniformly distributed. Sunlight and ultraviolet light were found to be similar in effects, in spite of the fact that ozone is formed only by the shorter wave-length ultraviolet light absent from sunlight.

The rate of oxidation of vulcanized rubber in ultraviolet light and air or oxygen increases with the time of vulcanization. It is greatly increased by extraction with acetone. It varies greatly with the kind of rubber, vulcanized crepe oxidizing far more rapidly than vulcanized Para rubber, probably because ultraviolet light penetrates the former much more readily than the latter.⁶⁸ The difference in the rate of oxidation of unextracted and extracted vulcanized rubber is probably closely related to the condition of the sulfur and to the absorption of ultraviolet light, for it is known that ultraviolet light is completely absorbed by a vulcanized mixture which reflected it before vulcanization and that carbon disulfide containing sulfur absorbs ultraviolet light while carbon disulfide alone transmits it. This suggests a means of determining whether sulfur is chemically combined or in solution and suggests that chemical combination occurs during vulcanization. The primary yellow products of oxidation in ultraviolet light are converted by boiling dilute sulfuric acid to the same brown substances which are obtained on oxidation in darkness at 70°C. The immediate onset of oxidation in ultraviolet light is in contrast to the induction period in oxygen alone. The gain in weight occurring during the oxidation in ultraviolet light ceases long before the oxygen reaches the proportion represented by C_8H_8O . The rate of oxidation of vulcanized rubber in ultraviolet light and air at 40° to 45°C. is about three times that in air at 70°C. in darkness.

Kirchhof⁶⁹ later used the ability of the natural water extract of raw rubber to reduce an ammoniacal silver nitrate solution at room temperature in detecting the effect of light on rubber. After a brief exposure to light, crêpe still reduces the reagent with dispersion of silver throughout the rubber, whereas water-extracted crêpe or crêpe bleached with sodium bisulfite does not reduce the reagent. After prolonged exposure crêpe no longer reduces the reagent, because light in conjunction with oxygen destroys the reducing substances (probably sugars). There is also a bleaching effect, perhaps because of the formation of hydrogen peroxide. Ultraviolet light has the same effect as sunlight, except that there is a yellowing instead of a bleaching, perhaps because of peroxide formation.

In sunlight and ultraviolet light, purified gutta-percha slowly turns yellow and on treatment with ammonia-silver nitrate turns brown because of peroxide formation. Samples of pale crêpe with no reducing action were immersed in solutions of hydroquinone, phenyl- α -naphthylamine and the commercial antioxidants, Parazone ND and MB, dried in darkness, and exposed to ultraviolet light. There was no visible change except with the phenyl-naphthylamine in which case yellowing occurred. On treatment with ammonia-silver nitrate, there was reduction with hydroquinone and Parazone, while with the phenyl- α -naphthylamine and Parazone MB, there was no reduction, even by the unexposed part. Since hydroquinone and Parazone have a marked protective action on rubber exposed to light, this action is related directly to the reducing power. The stability of hydroquinone and Parazone toward light accounts for the continued protective effect at low concentrations.

⁶⁸ Kirchhof, F., *Kautschuk*, 239, 256 (1927); *Chem. Abs.*, 21, 3766 (1927).

⁶⁹ Kirchhof, F., *Kautschuk*, 9, 70 (1933); *Chem. Abs.*, 27, 4126 (1933).

Dogadkin and Balandina⁷⁰ irradiated rubber with ultraviolet light under water in quartz flasks. Aqueous extracts were then prepared and tested for oxidation products which at 100°C. reduce gold salts to rose-colored colloidal gold. Unexposed pale crêpe and smoked sheet gave no reduction, but after ultraviolet irradiation they each reduced gold chloride. In each case on continued irradiation the concentration of colloidal gold increased to a maximum and then diminished. The electrical conductivity of the extracts, after diminishing slightly to a minimum after a certain period of irradiation, increased continuously.

Defries and Naunton⁷¹ investigated the effect of sunlight on the color of cured and uncured accelerated mixes. Rubber mixtures containing crêpe 100, zinc oxide 10, barium sulfate 100, and sulfur and accelerator (diphenylguanidine, di-*o*-tolylguanidine, triphenylguanidine, mercaptobenzothiazole, thiocarbanilide, aldehyde-ammonia, tetramethylthiuramdisulfide and zinc diethyldithiocarbamate) were exposed to ultraviolet light. With all accelerators, exposure before curing gave no visible effect, but, when cured, the previously exposed samples were much darker than ones not so treated before curing. These darker samples could not be lightened by irradiation. Ultraviolet light induces oxidation of the vulcanizates. When the samples were undercured, a second exposure to light intensified the darkening. The results indicate, first, that exposure of uncured samples causes a surface vulcanization, second, the discoloration is an effect of a surface overcure produced by normal vulcanization superimposed on an already slightly vulcanized surface and third, bleaching of vulcanizates by light results from oxidation, since it can be minimized by exposure in an inert gas and can be produced by oxidizing agents. When, however, there is an excess of vulcanizing agent to permit after-vulcanization, a subsequent exposure induces further darkening instead of bleaching.

ACCELERATED WEATHERING TESTS

Artificial aging of vulcanized rubber was thought by Pelizzola⁷² to be identical with natural aging, from both chemical and physico-mechanical points of view. Asano⁷³ directed experiments toward an understanding of the fundamental processes involved. As an aging test, he recommended that samples be maintained at 71°C. in a steady current of air and at the same time be exposed to ultraviolet light until the changes are of sufficient magnitude to compare the stress-strain curves and the chemical composition. By this test, rubber-insulated wire cracked after an hour, although it remained unchanged after fifteen hours in darkness.⁷⁴

It must be noted that light is but one of several aging factors employed in accelerated aging tests, although it is the only one requiring mention here. Jecusco⁷⁵ placed a Uviarc in the accelerating cabinet 7 cm. above the reel which held the samples of rubber so that its rays fell at right angles to the narrow part of dumbbell samples held by clips. The oven was of a standard construction 3 feet deep, 5 feet high and 4 feet wide, with walls filled with 2-inch asbestos and air insulation. It had a specially constructed wooden reel, 24 inches in diameter

⁷⁰ Dogadkin, B., and Balandina, V., *Kautschuk*, **9**, 146 (1933); *Rubber Chem. Tech.*, **7**, 18 (1934); *Chem. Abs.*, **28**, 4936 (1934).

⁷¹ Defries, R., and Naunton, W. J. S., *Trans. Inst. Rubber Ind.*, **4**, 298 (1928); *Chem. Abs.*, **23**, 2068 (1929).

⁷² Pelizzola, C., *Giorn. chim. ind. applicata*, **4**, 458 (1922); *Chem. Abs.*, **17**, 1559 (1923).

⁷³ Asano, K., *India-Rubber J.*, **70**, 307, 347, 389 (1925); *Chem. Abs.*, **19**, 3616 (1925).

⁷⁴ Asano, K., *Mem. Kyoto Univ.*, No. 3, 267, 1926; *Gummi-Ztg.*, **41**, 1576; *Chem. Abs.*, **21**, 2398 (1927). For other early tests, see also Jacobs, S., *Caoutchouc & gutta-percha*, **25**, 14,110 (1928) and Krahli, M., *Kautschuk*, **159**, 180 (1927); *Chem. Abs.*, **21**, 2816 (1927).

⁷⁵ Jecusco, F. P., *Ind. Eng. Chem.*, **18**, 420 (1926). Recent aging apparatus is described by Walter, P., *Rev. gén. caoutchouc*, **14**, No. 134, 26 (1937).

and 28 inches long, having eight arms and eleven wooden cross rods one inch in diameter forming an open reel of the squirrel-cage type. This revolved on a shaft at 26 r.p.m. Underneath a perforated floor plate were enough electric heating units to give a temperature of 50 to 100°C., automatically controlled by a thermostat. Underneath the floor plates on either side of the oven were large adjustable air shutters and baffle plates to admit the circulation of air through the heaters. There was also a top vent with damper control.

When both light and heat were used, a sample gave twice as much acetone-extract as after the heat test alone. In the heat test there was merely a pronounced darkening at the end of 144 hours, but with light and heat, the sample began to fog after three hours, a brownish tint began to appear at six hours, and after nine hours it was decidedly brown. After 21 hours the sample started to darken not unlike a sample heated alone for 144 hours. It gradually became darker up to 39 hours when it threw a purplish hue over the brown. This colored coating was insoluble in all common organic solvents and in caustic soda solution. Even after three hours, the surface was somewhat checked. This was pronounced at 39 hours. It began to crack at six hours. A decided stiffening became apparent at 18 hours and continued to the end of the test. The loss of weight was, however, decreased in this test.

Other rays than those shorter than the 2250Å (found active by Asano, who used only raw rubber) were effective in the aging of vulcanized rubber. Even sunlight was effective. Sunlight appeared to act in spurts. At 90°F. the first spurt from the cold Uviarc starts at the beginning of irradiation and continues until the breaking stress has been reduced from the initial 2260 to 1575 lbs. per square inch (fifteen hours) after which the deterioration is slow. At higher temperatures the spurts are more frequent and the delays shorter. The cause of these delays in the aging may be the formation of a protective coating. From filter experiments, it was concluded that green rays which have apparently no action on fresh rubber, have a tremendous effect on oven-aged rubber. Infrared rays showed an effect on both fresh and "activated" rubber. Apparently all rays have an action at some stage on the degradation of vulcanized rubber. The results seemed to indicate that light did not give a quantitative measure of the ability of rubber to withstand weathering.

Others, however, believed ultraviolet light to give a fair indication⁷⁶ of the ability of samples of raw or vulcanized rubber to withstand exposure to sunlight under natural conditions. The visible changes of individual samples are only relative and an adequate judgment of their aging properties requires the simultaneous exposure of samples of known aging properties. The ultraviolet light test is also useful in predicting the behavior of dyes in rubber.

Krahl⁷⁷ found ozonized air to have little effect on sharply bent rubber mixtures unless they were simultaneously exposed to ultraviolet light. Then they soon cracked at the bent sections. The resistance to such attack varies with different mixtures. In general, dark-colored mixtures crack sooner than light-colored ones, and overcured mixtures crack sooner than normally cured ones. In the aging test, Krahl exposed the samples intermittently to ultraviolet light so that their temperature did not rise to a point at which thermal changes become significant. He accomplished this by using a water-cooled rotating drum on which the radiation falls over one longitudinal section. The friction strength of insulating tapes in

⁷⁶ K. L., *Gummi-Ztg.*, 41, 417 (1926); *Chem. Abs.*, 21, 510 (1927).

⁷⁷ Krahl, M., *Kautschuk*, 159, 180 (1927); *Chem. Abs.*, 21, 2816 (1927).

this test⁷⁸ first increased with the time of exposure and then decreased progressively until it was but negligible. In comparative tests in which the samples were merely heated in air at 70°C., the strength decreased progressively from the beginning.

More complicated tests have been devised. In one,⁷⁹ during each revolution of a wheel about eight feet in diameter, the samples were successively submitted to immersion in water, desiccation by a hot or cold air blast, ultraviolet radiations, ozone, etc.

Yamazaki⁸⁰ exposed samples of vulcanized rubber to sunlight filtered through one of four glass plates transparent to 2900, 3130, 3300 and 4360Å, respectively. The effect of the unavoidable heating was studied in control experiments by air-heating at 70-71°F. in darkness for 150 hours. The color of vulcanized rubber became darker by air-heating, but when exposed to sunlight at 60-70°F. the change in color was far more remarkable. The higher the degree of vulcanization, the greater the change in color. Moreover, the rubber was hardened by the action of light. The shorter the wave-lengths and the higher the temperature, the sooner did hardening occur. The action of the rays of wave-length greater than 4300Å was very weak except in the case of overvulcanized rubber which was noticeably hardened. The acetone extract increased with the time of exposure, the rate of increase being less the longer the wave-lengths used. In some cases, the acetone extract reached a maximum and then decreased. It was considered that the increase in acetone extract was due principally to the oxidation of the rubber. The subsequent decrease, when observed, was attributed to the conversion of a part of the oxidized product into substances insoluble in acetone. The action of light and heat also caused a remarkable decrease in the free sulfur. The time of vulcanization of rubber-sulfur mixtures had a marked effect on the aging properties.

The deterioration due to sunlight was great even in winter and was very marked in the spring at 60°F. The outer layers of test-pieces exposed to sunlight were quite brittle and inelastic but the inner layers were still fairly good. Test-pieces subjected to Geer oven tests showed but little difference between the outer and inner layers.

Differences between the effects of sunlight and a quartz mercury arc were noted by Weightman⁸¹ in the case of vulcanized mixtures, particularly those which contained reclaimed rubber. Some samples of the latter which failed in service were comparatively resistant to ultraviolet rays. A violet carbon arc gave results more similar to those of sunlight. Temperature, humidity and air supply should be controlled during the test.

McKee and Depew⁸² found that overcured mixtures become surface checked sooner than the corresponding undercured mixtures in the light test, although the reverse was the case in darkness. Paraffin and zinc oxide retarded this action of light.

The varied conditions under which rubber is used make it particularly difficult to find any one suitable artificial aging test. Bierer and Davis⁸³ believed that

⁷⁸ Krahrl, M., *Gummi-Ztg.*, 42, 965 (1928); *Chem. Abs.*, 22, 1495 (1928).

⁷⁹ French office nationale des recherches et inventions, *Rev. gen., caoutchouc*, No. 29, 11 (1927); *Chem. Abs.*, 21, 1899 (1927).

⁸⁰ Yamazaki, T., *J. Soc. Chem. Ind. Japan*, 30, 804 (1927); *Brit. Chem. Abs.*, B, 615 (1928); *J. Soc. Chem. Ind. Japan*, 31, 233, 243 (1928); *Chem. Abs.*, 22, 3066 (1928); Yamazaki, T., and Okuyama, K., *J. Soc. Chem. Ind. Japan*, 32, 367B (1929); *Brit. Chem. Abs.*, B, 250 (1930); *Caoutchouc & gutta-percha*, 27, 15,016 (1930).

⁸¹ Weightman, H. E., *Rubber Age (N. Y.)*, 23, 75 (1928); *Chem. Abs.*, 22, 2290 (1928).

⁸² McKee, R. H., and Depew, H. A., *Ind. Eng. Chem.*, 20, 484 (1928).

⁸³ Bierer, J. M., and Davis, C. C., *Ind. Eng. Chem.*, 21, 1008 (1929). See also Karpinsky, Z., *Przemysł Chem.*, 21, 202 (1937); *Chem. Abs.*, 31, 8989 (1937).

neither the Fade-Ometer (see Chapter 32) nor the ultraviolet light tests truly duplicate the effects of sunlight.

In the aging of rubberized balloon fabrics, according to Barr,⁸⁴ there are essential differences between the effects of ultraviolet light and of tropical sunlight. Losses in tensile strength of the fabrics were similar, but though the permeability of the samples exposed to ultraviolet light remained unaltered, those exposed to sunlight became extremely permeable and their sulfuric acid contents became relatively large. Ultraviolet light caused a disproportionately great deterioration of the cotton, whereas tropical sunlight acted relatively rapidly on the rubber and sulfur with the formation of sulfuric acid which in turn attacked the cotton. Organic dyes and inorganic pigments protect the cotton from sunlight, lead chromate giving the best results.

Grafte⁸⁵ finds that in the light test the increase in acetone extract and the gain in weight are parallel up to an advanced stage of deterioration, so that the progress of the aging can be followed by the gain in weight. By the use of intermittent exposures, it was found that at certain stages of the aging process ultraviolet light accelerates a subsequent autoxidation in the air.

Tanaka, Kambara and Fujita⁸⁶ state that the original cold elongation of vulcanized rubber is increased by exposure to ultraviolet rays.⁸⁷

Ebonite that had been exposed under glass for fifteen years to light showed superficial cracking and masses of a whitish deposit.⁸⁸ The majority of samples showed a content of combined sulfur greater than that corresponding to the formula C_5H_8S . The exposure appeared to have caused oxidation of part of the caoutchouc to "resins," leaving a residue richer in sulfur. Certain of the samples containing organic softening ingredients such as palm pitch or carnauba wax had deteriorated less than the others.

Exposure of semi-ebonite to ultraviolet radiations⁸⁹ caused small increases in weight with the formation of a very thin hard and lustrous skin. Exposure outdoors also increased the weight and brought about surface changes. The effects of antioxidant both on exposure to ultraviolet rays and outdoors were relatively small.

Following an induction period, the electrical resistivity of the surface of low-grade loaded hard rubber and ebonite on exposure to light, air and humidity drops rapidly. It reaches a saturation point at about 10^7 to 10^8 ohms, after which it continues relatively slowly.⁹⁰ Ebonite, though initially superior to low-grade loaded hard rubber, deteriorated more rapidly and to a greater degree. After removal from the light, the resistivity of the low-grade loaded hard rubber increased slowly. The surface resistivity of ebonite was sensitive to the relative humidity during measurements, except during the induction and saturation stages. When the relative humidity during exposure was varied, there was found a maximum rate of deterioration of ebonite at 70-90 per cent relative humidity, indicating that both

⁸⁴ Barr, G., *Trans. Inst. Rubber Ind.*, **5**, 31 (1929); *Chem. Abs.*, **23**, 5350 (1929). Tests for rubber composition scales are described by Dock, E. H., *Trans. Inst. Rubber Ind.*, **13**, 160 (1937).

⁸⁵ Grafte, L., *Caoutchouc & gutta-percha*, **28**, 15,714, 15,797 (1931); *Chem. Abs.*, **26**, 622, 1152 (1932).

⁸⁶ Tanaka, Y., Kambara, S., and Fujita, H., *J. Soc. Chem. Ind. Japan*, **37**, 522 (1934); *Brit. Chem. Abs.*, **B**, 1071 (1934).

⁸⁷ For further general reviews of aging tests, see Garner, T. L., *Ind. Chemist*, **7**, 295 (1931); Moureu, C., Dufrasse, C., and Lotte, P., *Ind. Eng. Chem.*, **22**, 549 (1930); Jackson, H., *Trans. Inst. Rubber Ind.*, **10**, 292 (1934); *Chem. Abs.*, **29**, 3871 (1935); Carpenter, A. W., *India Rubber World*, **95**, No. 6, 39, 44, 48 (1937); Saito, S., *J. Soc. Rubber Ind. Japan*, **6**, 525 (1933).

⁸⁸ Scott, J. R., *Res. Assoc. British Rubber Mfrs.*, **5**, 2 (1936); *Brit. Chem. Abs.*, **B**, 338 (1936).

⁸⁹ Gibbon, P. A., *Trans. Inst. Rubber Ind.*, **10**, 494 (1935); *Chem. Abs.*, **29**, 6468 (1935).

⁹⁰ Church, H. F., and Daynes, H. A., *J. Rubber Research*, **6**, 13 (1937); *Chem. Abs.*, **31**, 5211 (1937).

dry and saturated atmospheres had a retarding effect. In artificial light (15 cm. from a 100-watt gas lamp), deterioration was slower than in bright north light, but, in the case of ebonite, the results were the same when expressed in standard hours measured by a photographic exposure meter. The low-grade hard rubber deteriorated relatively less rapidly in artificial light, probably because of a recovery of its resistivity value. Accelerated and artificial light aging tests cannot yet be accepted as criteria of true relative stabilities in sunlight.

Turner⁹¹ studied the influence on the sun-cracking of vulcanizates exerted by quantities of coloring matter too small to alter significantly the characteristics of the white base mixture. Inorganic and organic colors (both soluble and insoluble in rubber) including blue or black, red, green and yellow ones, were tested in two types of non-blooming white vulcanizate exposed under low stress (6 or 7 per cent elongation) to sunlight. In all cases, surface cracking took place much sooner when a coloring agent was present. Next to white vulcanizates, the blue ones were the slowest to crack. The resistance of the white vulcanizates was attributed to their ability to form a protective skin more readily than do the colored products. The coloring materials were thought to absorb wave-lengths which might otherwise be absorbed by the rubber and lead to the formation of the skin. A translucent vulcanizate absorbs more light than does a white one and therefore forms a protective skin more readily than does a corresponding opaque one. This was shown by the fact that a vulcanizate containing titanium dioxide cracked sooner than a corresponding one containing an equal volume of barium sulfate and having a more pronounced film. This may explain the beneficial effect of magnesium carbonate.

PROTECTION OF RUBBER

According to Schopper,⁹² solutions of coumarin derivatives, *e.g.*, a 1-per cent solution of dimethylamino-methylcoumarin, may be used to absorb ultraviolet rays and protect the fabric of balloons from damage by sunlight. Jakowsky⁹³ calls attention to the opaqueness of the carbon black used as a reinforcing agent in rubber and notes the general belief that this property affords rubber of greater durability by preventing the penetration of light, especially ultraviolet rays, into rubber.

Shepard, Krall and Morris⁹⁴ attempted to determine the influence of various compounding ingredients, including fillers, softeners, accelerators, and an anti-oxidant, on sun-checking. They stretched the rubber to an elongation of 12.5 per cent and obtained checking of susceptible samples within 24 hours, although unstretched samples were not checked for months when exposed to sunlight. Dumbbell strips, 5 mm. thick, stretched on frames, were hung by ropes from the roof where they could revolve in the wind. It was concluded that, through the proper selection of rubbers, reclaim and compounding ingredients, it is possible to reduce to a marked extent the tendency of rubber products to check and crack. The maximum results from a checking standpoint would be obtained by using only those materials in compounding that are protective in their action. Unfortunately, however, selective pigmentation cannot usually be resorted to without the sacrifice of desirable physical properties. Carbon black, for example,

⁹¹ Turner, H., *Trans. Inst. Rubber Ind.*, 10, 21 (1934); *Chem. Abs.*, 28, 7591 (1934).

⁹² Schopper, T., *Gummi-Ztg.*, 29, 1250 (1915); *Z. angew. Chem.*, 28, Ref. 644 (1915); *J. Soc. Chem. Ind.*, 356 (1916).

⁹³ Jakowsky, J. J., *Bureau of Mines Tech. Paper* 351 (1924); see also Bradshaw, H., *Ind. Eng. Chem.*, 19, 1110 (1927).

⁹⁴ Shepard, N. A., Krall, S., and Morris, H. L., *Ind. Eng. Chem.*, 18, 615 (1926).

has no protective action, and even in small quantities offsets the protective action of other pigments; but for tread stocks this pigment is highly desirable for toughness, resistance to tear and abrasion. Other characteristics, such as the blooming of certain protective materials, make their commercial application very difficult. There is little difference between the accelerators triphenylguanidine, diphenylguanidine and methylene-*p*-toluidine. Benzidine (the only antioxidant tested) has to be added to the extent of 3.6 per cent to give complete protection for a week. The solubility of a material in rubber plays a prominent part in its value as a protective agent. Mineral rubber and other asphaltic substances have no beneficial effect. Rosin and pine pitch are detrimental. Vegetable oils have little effect. Paraffin has a stronger protective action than Vaseline, but more than 2 per cent is necessary for complete protection. A light engine-oil is inferior to Vaseline. Crude Montan wax is but little if any better than asphaltic softeners. When refined, it is intermediate between Vaseline and paraffin. Zinc oxide and lithopone do not protect to the same extent as whiting and clay which are of low covering power. Low-grade off-color rubbers are not more susceptible to sun-checking than are high-grade rubbers. A white stock loses much more in resistance when made gray or black.

Dyestuffs capable of absorbing ultraviolet light were added by Porritt and Dawson⁹⁵ who also used polyphenols and aminophenols as antioxidants. Lister found dragon's blood resin to offer no protection against oxidation in cured rubber proofing exposed to the weather and to ultraviolet light.⁹⁶

Preservative paints or coatings for application to rubber goods may be made with a medium capable of swelling the rubber and a material, such as mineral rubber, to increase the viscosity and afford some mechanical protection. Small quantities of antioxidants, such as aldol- α -naphthylamine, and of yellow or red substances such as Oil Red S may be added.⁹⁷

Henri⁹⁸ stated that litharge and antimony sulfide accelerate the changes produced by ultraviolet rays. Copper salts, even in traces, are bad,⁹⁹ while powdered glass, according to Ditmar,¹⁰⁰ protects in direct proportion to the amount present. Zinc oxide accelerates oxidation but not in any direct relation to its percentage.

Kreusler and Budde¹⁰¹ dipped vulcanized rubber articles into a paraffin bath at 100°C. to render them resistant to light and air. Himmelbauer and Co.¹⁰² used Vaseline or ceresin wax. Ahrens¹⁰³ stated that in 1899 he added ceresin to a tread stock on the mixing mill and then exposed tires with half and half tread, one-half containing ceresin and the other not. The protective action observed in the presence of ceresin was ascribed to the chemically inert bloom or coating of ceresin. Chertoff¹⁰⁴ uses certain vegetable oils, including palm, rosin, pine and turpentine oils, with resins (dammar, rosin, copal), to prevent rapid deterioration and hardening of rubber with age. Paraffin, mineral and other non-drying oils have also been suggested by Repony.¹⁰⁵

Mazurek and Josse¹⁰⁶ recommended that fabric for the Gordon Bennett Cup

⁹⁵ Porritt, B. D., and Dawson, T. R., British P. 269,745, May 25, 1926, to Research Association of British Rubber and Tyre Manufacturers; *Chem. Abs.*, 22, 1498 (1928).

⁹⁶ Lister, W. N., *J. Soc. Chem. Ind.*, 46, 220T (1927); see also Kelly, A., Taylor, B. S., and Jones, W. N., *Ind. Eng. Chem.*, 20, 296 (1928).

⁹⁷ Porritt, B. D., Dawson, T. R., and Research Association of British Rubber and Tyre Mfrs. British P. 299,169, Sept. 29, 1927; *Brit. Chem. Abs.*, B, 937 (1928).

⁹⁸ Henri, V., *Caoutchouc & gutta-percha*, 7, 4372 (1910); Matter in this paragraph is derived from Shepard, N., Krall, S., and Morris, H.⁹⁴

⁹⁹ Bing, K., *Kolloid-Z.*, 4, 232 (1909).

¹⁰⁰ Ditmar, R., *Gummi-Ztg.*, 21, 243 (1906).

¹⁰¹ Kreusler and Budde, German P. 18,740, Aug. 26, 1881.

¹⁰² Himmelbauer and Co., *Chem. Ztg.*, 36, 1441 (1912).

¹⁰³ Ahrens, F., *Chem. Ztg.*, 36, 1441 (1912).

¹⁰⁴ Chertoff, G. J., U. S. P. 1,379,743, May 31, 1921; *Chem. Abs.*, 15, 3414 (1921).

¹⁰⁵ Repony, D., *Rubber Age (N. Y.)*, 5, 5 (1919).

balloons be colored red or yellow to protect the mixture from light, and also that it be impregnated on both sides with Revertex mixture. Coe¹⁰⁷ combines chlorophyll green with rubber in such manner as to exclude all wave-lengths of light except those transmitted between 5270 and 6500A.¹⁰⁸

Bonding Rubber to Other Materials. Livings and Lacey¹⁰⁹ described a method of bonding unvulcanized rubber to metal, glass, or ebonite, by preparing a bonding surface on the rubber by exposure to ultraviolet rays. Rubber so treated may also be used to bond together materials of dissimilar or similar nature, such as metal and wood or metal and metal. The rubber is finally subjected to pressure and vulcanization.

In joining vulcanized rubber compositions to metals, glass, molded phenol condensation products, hard rubber, etc., Morse¹¹⁰ inserts a sheet of rubber composition containing a vulcanizing agent such as sulfur, zinc oxide and glue. To reduce tackiness one surface of it is previously exposed to light from a carbon arc for a period sufficiently beyond that at which the tackiness of the rubber may be increased. It is inserted between the materials to be joined, with the unexposed surface of the sheet adjacent to the first-mentioned rubber composition and the sheet of rubber composition is vulcanized in place.

Chlorinated Rubber. In a patent for the production of plastic products from india-rubber, Dyche-Teague¹¹¹ states that rubber which has been thoroughly depolymerized by milling is dissolved in a suitable solvent (carbon tetrachloride or benzene) and then chlorinated. Additional depolymerization prior to chlorination may be effected by subjecting the solution to actinic light. Distillation removes the solvent and hydrogen chloride. The reaction product, which may contain 50 to 60 per cent of chlorine, forms fluid solutions which afford alkali- and acid-resistant lacquers or paints.

It has been said that chlorinated rubber prepared in the laboratory, besides being resistant to acids, alkalies, corrosive salts and strong oxidizing agents, is unaffected by ultraviolet light.¹¹²

In the preparation of chlorinated rubber¹¹³ chlorine is introduced into solutions of rubber of a concentration of 2 per cent or less and of low viscosity, and the resulting rubber chloride solution is gradually poured into hot water in which is immersed a disintegrating apparatus whereby the solvent is evaporated and the chloride is reduced to the granular state. Prior to adding it to water, the solution may be reduced in viscosity by standing, exposure to light, or by the addition of alkali. The time for chlorination is also greatly reduced by irradiation.¹¹⁴ Subsequent to chlorination, the product may be further irradiated (sunlight or mercury arc) until the desired viscosity is reached.

By the use of ultraviolet rays, Floresco¹¹⁵ increases the concentration of rubber

¹⁰⁸ Mazurek, S., and Josse, Z., *Przemysl Chem.*, **18**, 481 (1934); *Brit. Chem. Abs.*, **B**, 144 (1935).

¹⁰⁷ Coe, M. R., U. S. P. 2,042,333; *Chem. Abs.*, **30**, 5071 (1936).

¹⁰⁶ Note also for the effects of other light filters, Margaritov, V., *J. Rubber Ind. (U.S.S.R.)*, No. 1, 42, 1936.

¹⁰⁹ Livings, G., and Lacey, B., British P. 418,035, 1934, to Dunlop Rubber Co., Ltd.; Canadian Patent 354,930; *Chem. Abs.*, **29**, 2395 (1935).

¹¹⁰ Morse, D. S., U. S. P. 2,047,880, July 14, 1936; *Chem. Abs.*, **30**, 6240 (1936).

¹¹¹ Dyche-Teague, F. C., British P. 305,968, Sept. 13, 1927; *Brit. Chem. Abs.*, **B**, 334 (1929).

¹¹² Kojima, K., and Toyabe, Y., *J. Soc. Chem. Ind. Japan*, **36**, 236B (1933); *Chem. Abs.*, **27**, 3852 (1933).

¹¹³ British P. 400,898, Nov. 2, 1933, to Chemische Fabrik Buckau; *Chem. Abs.*, **28**, 2219 (1934).

¹¹⁴ French P. 768,157, Aug. 1, 1934, to Chemische Fabrik Buckau; *Chem. Abs.*, **29**, 640 (1935); Mollney, E., German P. 660,524, May 28, 1938; *Chem. Abs.*, **32**, 6905 (1938).

¹¹⁵ Floresco, N., French P. 768,632, Aug. 10, 1934; *Chem. Abs.*, **29**, 640 (1935); Floresco, N., and Pfrunder, N., French P. 787,212, Sept. 19, 1935.

solutions to be halogenated without increasing their viscosities. The rays were said also to activate the halogenation and increase the stability of the products formed.

Buisov, Molodenskii and Mikhaïlov¹¹⁶ stated that a chlorinated rubber containing 51.1 per cent of chlorine did not disintegrate in ten hours of exposure to ultraviolet rays. A freshly prepared rubber solution which had been irradiated for six hours gave after fifty minutes of chlorination a product with 68.2 per cent of chlorine. On the other hand, a solution of rubber containing 10 per cent of benzoyl peroxide after irradiation for eight hours and chlorination for one hour gave a product containing only 40.2 per cent of chlorine. This was unstable to light and heat. They conclude that the rubber must be disaggregated but not oxidized if it is to yield a good chlorinated product.¹¹⁷ In discussing the use of chlorinated rubber in lacquers, Rosenthal and Schulze¹¹⁸ state that because of the action of ultraviolet rays upon this product, only pigmented films are of practical use. They recommend titanium dioxide, chromium trioxide green, iron oxide pigments and graphite. Among other substances proposed¹¹⁹ to be added in amounts up to 5 per cent to increase the light-stability of chlorinated rubber are dicyclohexylamine, ditetrahydrofurfurylamine, methyleneaminoacetonitrile, cyclohexylamine-formaldehyde, cyclohexylamine acetonitrile, tetramethylthiuramdisulfide, diphenylguanidine and dihydroxydiphenylpropane. Campbell and Reed¹²⁰ find 4-hydroxy-2-methyl-N-phenylmorpholine the best of six new N-phenylmorpholines in protecting rubber from staining after artificial illumination. Baxter¹²¹ finds that plasticizers absorbing wave-lengths shorter than 3100A, such as dibutyl phthalate, stabilize chlorinated rubber and protect it from discoloration by light. Ethylene oxide is also recommended by Becker.¹²²

Ultraviolet light is used by Laurin and Bidot¹²³ in the preparation of a substitute for rubber. To a mixture of glue as hydrogel with gum tragacanth and wood dust there are successively added: glycerol, vegetable oils, such as castor or colza oil, a resinate treated with formaldehyde, a resin solution such as a solution of Bakelite in naphtha, potassium dichromate, and potassium alum. Each addition is followed by a homogenization and the mass is kept in darkness from the time the potassium alum is added for a variable time subsequently. Pieces of the product obtained are exposed to ultraviolet rays to effect stabilization.

¹¹⁶ Buisov, B. V., Molodenskii, V. S., and Mikhaïlov, N. I., *J. Rubber Ind. (U.S.S.R.)*, **11**, 44 (1934); *Chem. Abs.*, **29**, 953 (1935).

¹¹⁷ For the action of ultraviolet on chlorinated rubber, see also *Synthetic and Applied Finishes*, 65 (1934).

¹¹⁸ Rosenthal, L., and Schulze, G., *Farben-Chem.*, **5**, 53 (1934); *Brit. Chem. Abs.*, **B**, 636 (1934).

¹¹⁹ British P. 437,304, Oct. 22, 1935, to Wingfoot Corp.; *Chem. Abs.*, **30**, 2422 (1936). British P. 479,464, Feb. 7, 1938; *Chem. Abs.*, **32**, 5256 (1938).

¹²⁰ Campbell, A. W., and Reed, M. C., *Ind. Eng. Chem.*, **28**, 656 (1936).

¹²¹ Baxter, J. P., *Chemistry and Industry*, 407 (1936); *Chem. Abs.*, **31**, 4531 (1937).

¹²² Becker, W., *Rubber Tech. Conf., London, Preprint No. 96*, May, 1938; *Chem. Abs.*, **32**, 8192 (1938).

¹²³ Laurin, L., and Bidot, E., U. S. P. 1,969,932, Aug. 14, 1934; *Chem. Abs.*, **28**, 6348 (1934).

Chapter 32

Textiles, Paper and Dyestuffs

Coarse yarns are less affected by light than are fine ones, because in the former the outer layers protect the inner strands.¹ Of the various fibers, Barr found silk to be more affected by light than cotton, but wool much less than either. Artificial silk is affected less than cotton.

Simola² found that exposure to sunlight through a double glass window for five warm months reduced the tensile strength of cotton 17.8 and of wool 7.3 per cent. The stretching properties were reduced an average of 12 per cent for cotton yarn and 37.7 per cent for worsted yarn. Fine-fibered wool suffered more than coarse-fibered.^{2a}

Expressed as the hours of sunshine required to cause a loss of 50 per cent in tensile strength, the order of deterioration of various textile fibers is as follows: silk (200), jute (400), artificial silk (900), cotton (940), flax (990), hemp (1100), raw wool (1120), chromed wool (1900). In this evaluation, the varying thicknesses of the textiles were not taken into account.³

Moisture, contrary to previous opinions, favors the deterioration, especially in the case of wool and bast fibers. The purer the atmosphere, the less is the destruction.

Waentig⁴ found the tearing strength of wool practically unaffected by sunlight or by rays from a quartz mercury lamp, the washed fibers being slightly more sensitive than the raw wool. Carver⁵ recommended ultraviolet radiations for testing fabrics used in automobiles.

It has been proposed to increase the resistance of textiles to ultraviolet light and water⁶ by subjecting them to the successive action of a tanning solution containing a wetting agent (5 per cent catechu and 5 per cent Tetraconite, a mixture of Turkey red oil, pyridine and tetrachloroethane), a mordanting solution (5 per cent lead acetate) and an oiling solution containing an aldehyde or ketone (5 per cent linseed oil in tetrahydronaphthalene with 2 per cent paraldehyde) to control the rate of oxidation during drying.

Cotton and Cellulose. Little is yet known as to the wave-lengths which are required for the destruction of cotton or cellulose. Barr⁷ maintained it to be

¹ Barr, G., *Trans. Faraday Soc.*, **30**, 284 (1924); Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923).

² Simola, E. J., *Teknillinen Aikakauslehti*, **23**, 326 (1933); *Chem. Abs.*, **28**, 647 (1934), *Acta Fennica*, **6A**, 126 (1933).

^{2a} Mercerized cotton lost 13.7 per cent in tensile strength and 27.3 per cent in elasticity.

³ Sommer, H., *Chem. Ztg.*, **51**, 777 (1927). Later, with Heermann, P., *Leipzig Monats. Textilind.*, **40**, 207 (1925) the order is given as: mineral weighted silk, raw silk, jute, raw and bleached cotton, raw wool, mercerized cotton, nitro- and viscose rayons, chromed wool, bleached flax yarn, cuprammonium rayon, raw flax yarn.

⁴ Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923). See also *J. Soc. Chem. Ind.*, **39**, 512A (1920); Vignon, L., *Ibid.*, **482A**; **42**, 825A (1923).

⁵ Carver, W. L., *Automotive Industries*, May 8, 1011 (1924).

⁶ British P. 263,102, Nov. 4, 1926, to Albert Meyer-Sans Bocuf Co.; *Brit. Chem. Abs.*, **1927B**, 746.

⁷ Barr, G., *Trans. Faraday Soc.*, **20**, 284 (1924).

⁸ Kauffmann, H., *Textilber.*, **7**, 617 (1926); *Chem. Abs.*, **20**, 3352 (1926).

due chiefly to wave-lengths shorter than 4000A. Kauffmann⁸ finds the region about 3500A probably effective, and states that visible light is without action.

Notwithstanding a considerable amount of work, the question as to whether an oxidation is involved cannot yet be said to have been definitely settled. Dyer and Dorée,⁹ who reviewed some of the earlier observations, concluded that ultraviolet rays convert cellulose into oxycellulose with complete loss of tensile strength, a view shared by Barr,¹⁰ and by Aston.¹¹

A new point of view was introduced by Kauffmann,¹² who believed the deterioration to occur independently of the presence of oxygen and without any change in weight. He concluded that the recognized formation of oxycellulose is preceded by the production of a compound "photocellulose," the formation of which does not involve oxidation. Like oxycellulose, the "photocellulose" reduces silver salts or Fehling's solution and shows a yellow color with caustic soda and phenylhydrazine. It is soluble in sodium hydroxide solution and has the formula $C_6H_{10}O_5$.

The action of ultraviolet light during the sun bleaching of cotton leads to the production of "photocellulose," the formation of which can be followed by a method involving the use of potassium permanganate. In cotton fabrics exposed for 45 days, 1 to 2 per cent of "photocellulose" is produced. The observed increased affinity of the exposed cotton for methylene blue was not, however, ascribed by Kauffmann to the presence of "photocellulose." This view is accepted by Sommer.¹³

Barr and Hadfield,¹⁴ however, concluded that an oxidation is involved. No significant change took place when strips of cotton cloth were exposed for six months to sunlight in sealed glass tubes containing hydrogen or about two-thirds saturated with water vapor. Similar exposure in tubes containing oxygen resulted in a considerable loss of strength, an increase in reducing power as shown by the copper number, and the production of carbon dioxide and carbon monoxide and perhaps hydrogen. The reaction was more rapid in the presence of moisture. There was a rough parallelism between the copper number and the quantity of carbon dioxide produced. With increase in the time of exposure, there was a continuous decrease in strength and of the viscosity of cuprammonium solutions prepared from the exposed cotton. The methylene blue absorption by the cotton showed first a fall and then a slow rise. In general, the modification of cotton produced by the light corresponded to that formed by mild oxidation with chlorine water. Cotton cloth previously steeped in 0.001N sulfuric acid is more highly reducing and shows a greater production of carbon dioxide under the same conditions of exposure. Precipitation of ferric hydroxide on the cotton before exposure results in an increased attack by the light, but lessens the formation of carbon dioxide.

These workers recognized, however, that at least two reactions may occur during the exposure of cotton to sunlight. Both are accompanied by a loss of strength and the development of reducing power. One reaction, however, produces much less carbon dioxide than the other, and is catalyzed by iron.

⁸ Dyer, J., and Dorée, C., *J. Soc. Dyers Colourists*, 33, 17 (1917); *Chem. Abs.*, 11, 1753 (1917). See also Scheurer, A., *Bull. Soc. Mulhouse*, 80, 324 (1912). A recent review is given by Cady, W. H., *Am. Dyestuff Rept.*, 27 (*Proc. Am. Assoc. Textile Chem. Colorists*), p. 325 (1938); *Chem. Abs.*, 32, 5632 (1938).

¹⁰ Barr, G., *Trans. Faraday Soc.*, 20, 284 (1924).

¹¹ Aston, F. W., Report on the Action of Sunlight on Aeroplane Fabrics T1019, British Advisory Committee for Aeronautics, 1917.

¹² Kauffmann, H., *Textilber.*, 7, 617 (1926); *J. Soc. Chem. Ind.*, 817 (1926); *Chem. Abs.*, 20, 3352 (1926).

¹³ Sommer, H., *Chem. Ztg.*, 51, 777 (1927).

¹⁴ Barr, G., and Hadfield, I. H., *J. Textile Inst., Special Issue*, 18, 490 (1927); *Chem. Abs.*, 22, 2062 (1928).

The deterioration of linen also appeared to be the result of oxidation. Loss of strength occurred most rapidly in oxygen, less so in air, and was negligible in hydrogen, carbon dioxide or a vacuum.

According to Sharvin and Pakshver,¹⁵ exposure of bleached, ether-extracted, washed and dried cotton in sealed tubes with oxygen to sunlight showed a simultaneous formation of oxycellulose, carbon dioxide and water. During the earlier part of the process, there seemed to be a definite relation between the amounts of carbon dioxide and of oxycellulose formed, although it could not be expressed stoichiometrically. Upon continued exposure, the carbon dioxide formation decreased, but the oxycellulose appeared to undergo a further oxidation. In addition to the formation of carbon dioxide and water, there were produced compounds which had the odor of furfural but did not give its reactions. The fabric lost both in strength and in weight.

Ditz¹⁶ concludes that more work is necessary to explain the mechanism of the degradation of cellulose, an especially important reaction in the "grass-bleaching" of fabrics. Dumas¹⁷ reviews the analytical methods employed in such investigations.

It has recently been noted¹⁸ that the sorption of iodine from the vapor phase by cotton is greater after the cotton has been irradiated by ultraviolet light. Williams¹⁹ observed that cotton or viscose yarns when deteriorated by excessive bleaching or ultraviolet irradiation, lose much of their remaining strength, when wet. The ratio between wet strength and air-dry strength appeared to be a function of the degree of deterioration.

When exposed to the quartz mercury-vapor lamp, cotton hairs lose strength at a constant rate until the tendering amounts to about 40 per cent; the rate then diminishes.²⁰ Over a small range, the rate of tendering is proportional to the intensity of the light. Cotton hairs of different origin exhibit specific differences in their susceptibility to light tendering. The proportional loss of strength of yarns is about half that of hairs fully exposed under the same conditions, the hairs in the yarns being tendered to the same extent as the yarns. Bleached cotton is more rapidly tendered than raw. Material dyed with chrome green is much more resistant than the undyed scoured material. Ferric hydroxide has a slight protective action. Cloth-dyed mineral khaki is as resistant as the chrome-dyed material, the effect being such as to extend the life of fabrics subject to strong illumination to as much as five or six times that of untreated materials. Organic dyes modify the rate of tendering of cotton by light, some favorably and others unfavorably, but the effect is never as large as that of chromium hydroxide.

Experiments conducted for the British Government indicated²¹ that heavy cotton and linen tent fabrics are much less affected by sunlight than are the light and less exposed fabrics used in airplane and airship construction. Although such pigments as lead chromate diminish the deterioration by light, others, such as the stannates, tungstates and sulfides frequently used in fire proofing, accelerate it. Waterproofing frequently, but not always, has a beneficial action, depending on the process and materials used, the climatic conditions and the exposure.

¹⁵ Sharvin, V. V., and Pakshver, A., *Z. angew. Chem.*, **41**, 1159 (1928); *Chem. Abs.*, **23**, 3080 (1929).

¹⁶ Ditz, H., *Z. angew. Chem.*, **40**, 1476 (1927).

¹⁷ Dumas, M. J., *Rev. gen. mat. color.*, **41**, 149 (1937).

¹⁸ Beutel, E., and Kutzelnigg, A., *Monatsh.*, **64**, 41 (1934); *Chem. Abs.*, **28**, 3591 (1934).

¹⁹ Williams, J. G., *J. Soc. Dyers Colourists*, **48**, 167 (1932); *Chem. Abs.*, **26**, 4477 (1932).

²⁰ Cunliffe, P. W., Farrow, F. D., and Midgley, E., *J. Textile Inst.*, **19**, 169T (1928); *Brit. Chem. Abs.*, **B**, 563 (1928).

²¹ Hunter, J. A., *Textile World*, **69**, 309, 315 (1926); *Chem. Abs.*, **20**, 827 (1926).

After 500 hours in sunlight, 35 white and dyed cotton fabrics tested by Grimes²² showed losses in breaking strength of 18 to 49 per cent in the warp and 34 to 65 per cent in the filling. The mercerization of the Everfast suitings and broadcloths tested increased their resistance to tendering. In eight of fifteen dyed fabrics tested, less breaking strength was lost than in undyed fabrics. The time of exposure had far more effect on the loss of strength than had the temperature and relative humidity. Spectrophotometric analysis showed that sunlight affected the color of all white and dyed fabrics tested. The white ones became increasingly yellow with increased exposures.

The resistance of "tobacco cloth" to sun and rain may be improved by letting an acidulated solution of lead acetate penetrate it and then treating it with a solution of sodium dichromate so as to form lead chromate on the fibers.²³

Anthracene yellow GC and Chrysoidine have been found unsatisfactory for the protection of cotton from deterioration by light.²⁴

Cotton and viscose silk materials dyed with one of a large number of orange and yellow vat dyes (Indanthrene Yellow G and Alizaranthrene Yellow 6R excepted) if exposed to light and air immediately after dyeing while the dye is in its leuco condition, become tendered by oxidation.²⁵ The dye itself may also be simultaneously oxidized, with consequent partial or complete decolorization. If a second dye is present (especially Ciba Blue 2B), this may be oxidized in preference to the cotton or the first dye. These effects also are produced when the dyed fabric is oxidized in darkness before exposure to sunlight or a Fade-Ometer, but are not produced if again washed before exposure. Tendering occurs if the washed fabric is further impregnated with a dilute solution of caustic soda containing sodium hyposulfite or hydrogen peroxide and then exposed to light and air. By means of the starch iodide test it was shown that an active oxidizing agent, probably hydrogen peroxide, was formed during the oxidation of cotton dyed with Cibanone Yellow R. Certain direct dyes, including Diamine Fast Yellow and Chlorazol Fast Orange R, behave similarly to vat dyes in promoting tendering. The tendering of cotton when so exposed is rapid and may be serious in large-scale dyeing. For example, cotton fabrics lifted successively five times (ten minute exposure each time) from the dye liquor and exposed to light and air while being dyed with 20-per cent Cibanone Orange R had copper numbers of 0.2, (original fabric), 0.3, (dyed fabric not exposed), and 0.7, 1.3, 1.5, 1.7 and 1.75 (after five successive exposures). Viscose silk is particularly susceptible to tendering under these conditions. The destructive action of sunlight is not appreciably affected by transmission through plate glass a quarter of an inch thick or didymium glass opaque to yellow light.

A fading product of Ciba Blue 2B dyed on cotton, isolated by Scholefield, Hibbert and Patel,²⁶ appeared to be dibromoisatin. The fading products from cotton dyed with methylindigo gave the reactions of *o*-methylisatin. Hibbert²⁷ also impregnated calico, wool and cellulose acetate silks with 1,2,4-trihydroxyanthraquinone Purpurin. After 60 hours of exposure to the Fade-Ometer, a substance was extracted by carbon tetrachloride which was found to be a mix-

²² Grimes, M. A., *Texas Agr. Sta., Bull.* 506, 5 (1935); *Chem. Abs.*, 30, 291 (1936).

²³ Rhodes, G. H., U. S. P. 2,026,190; *Chem. Abs.*, 30, 1247 (1936).

²⁴ Kauffmann, H., *Textileber.* 7, 617 (1926); *Brit. Chem. Abs.*, 1926B, 817.

²⁵ Scholefield, F., and Patel, C. K., *J. Soc. Dyers Colourists*, 44, 268 (1928); *Brit. Chem. Abs.*, B, 811 (1928); *J. Soc. Dyers Colourists*, 45, 175 (1929); *Chem. Abs.*, 23, 4824 (1929).

²⁶ Scholefield, F., Hibbert, E., and Patel, C. K., *J. Soc. Dyers Colourists*, 44, 236 (1928); *Chem. Abs.*, 22, 3780 (1928).

²⁷ Hibbert, E., *J. Soc. Dyers Colourists*, 45, 204 (1929); *Chem. Abs.*, 23, 4824 (1929).

ture of phthalic acid and phthalic anhydride. Impregnation of calico with phthalic acid and its anhydride followed by exposure to the Fade-Ometer and extraction with alcohol and carbon tetrachloride was found to increase its affinity for methylene blue. Tables showing the manner in which various dyes catalyze the tendering action of sunlight on cotton have been given by Vashist.²⁸

Haller and Wyszewianski²⁹ investigated the sensitization of the photodecomposition of cotton by a series of vat dyes by exposing 25 per cent³⁰ dyeings on 10 gm. of heavy cotton calico to sunlight at a 45° angle to the south under 2 mm. of Ultravit glass. The loss of tensile strength was 9 per cent in white bleached calico after 130 normal bleaching hours. When treated with various anthraquinone intermediates, the corresponding losses were: anthraquinone, 27 per cent; 2-methylanthraquinone, 46 per cent; 1-chloroanthraquinone, 32 per cent; 2-chloroanthraquinone, 41 per cent; 1-aminoanthraquinone, 17 per cent; 2-aminoanthraquinone, 18 per cent; anthraquinone-1-sulfonic acid, 13 per cent and anthraquinone-2-sulfonic acid, 20 per cent; anthraquinone-1,5-disulfonic acid, 24 per cent. Graphs showed a decrease of as much as 40 per cent in the tear strength of cotton dyed with certain anthraquinone dyes after only 79 normal bleach hours, the dyeings varying from 0.05 to 1.0 per cent. Henk³¹ believes that in such cases the deterioration involves oxidation. It depends on the temperature, fiber structure and the presence of hydroxyl, amino or imino groups. The destructive process is hastened by such catalysts as the metal compounds in sizes and after-treatment, particularly chromium and copper salts, impure water containing manganese and nickel, and the titanium dioxide used in the manufacture of delustered rayons.

A method of producing light and elastic threads or cellulose cloths consists in impregnating them with the chlorates, bromates or iodates of metals of the second periodic group. These, under the influence of photoactive rays (but not ordinary light) degrade the fibers.³²

Pacini³³ has made the claim that the tensile strength of cellulosic materials such as cotton may be actually increased by subjecting it to ultraviolet radiation controlled in a special manner to prevent the formation of detectable oxycellulose.³⁴

Paper and Wood Pulp.³⁵ The bleaching of wood pulp, paper products or cotton textiles by chlorine is accelerated both by light and by increased temperatures. It is usually cheapest to depend upon the thermal reaction alone, but in certain cold climates where fuel is expensive, attempts have been made to employ artificially produced ultraviolet light for aiding the process. Escourrou³⁶ investigated the accelerating effect of a mercury-vapor lamp. Although the process could be carried out at a lower temperature, more chlorine was used, owing to the

²⁸ Vashist, S. D., *Indian Textile J.*, **42**, 376 (1932); *Chem. Abs.*, **27**, 192 (1933).

²⁹ Haller, R., and Wyszewianski, L., *Melliand. Textilber.*, **17**, 45, 138, 217, 325 (1936); *Chem. Abs.*, **30**, 6566 (1936).

³⁰ Wahl, A., [*Rev. gen. mat. color.*, **38**, 217 (1934); *Chem. Abs.*, **28**, 4910 (1934)] links the destructive action of the dyes with an absorption band at about 3300 to 3700 Å.

³¹ Henk, H. J., *Monatschr. Textilind.*, **51**, 186 (1936); see also E. Baur, *Helv. Chim. Acta*, **20**, 879 (1937).

³² French P. 803,145, Sept. 23, 1936, to Comptoir des textiles artificiel, *Chem. Abs.*, **31**, 2837 (1937).

³³ Pacini, A. J., U. S. P. 1,948,276, Feb. 20, 1934, to Millprint Products Corp.; *Brit. Chem. Abs.*, **B**, 1053 (1934).

³⁴ For the absorption of cellulose films in the extreme ultraviolet (8000 Å.), see O'Bryan, H. M., *J. Opt. Soc. Am.*, **22**, 739 (1932). It has been shown that the change in absorption of alkali cellulose during xanthogenation may afford a method for following the progress of the process. Atsuki, K., and Sobue, H., *J. Soc. Chem. Ind. Japan*, **36**, Suppl. binding, 589 (1933); *Chem. Abs.*, **28**, 710 (1934).

³⁵ Data on the absorption spectrum of lignin have been given by Herzog, R., and Hilmer, A., *Ber.*, **64B**, 1288 (1931); *Papier Fabr. Tech. Wiss. Teil*, **30**, 205 (1932); **29**, 4-5; *Chem. Abs.*, **26**, 4309 (1932); Hilmer, A., *Ber.*, **66B**, 1600 (1933); Hägglund, E., and Klingstedt, F. W., *Z. physik. Chem.*, **152A**, 295 (1931); Stamm, A. J., Semb, J., and Harris, E., *J. Phys. Chem.*, **36**, 1574 (1932).

³⁶ Escourrou, R., *Chimie et industrie*, **19**, 989 (1928); *Brit. Chem. Abs.*, **B**, 168 (1929); *Pulp Paper Mag. Canada*, **26**, 1549 (1928); *Chem. Abs.*, **22**, 4791 (1928).

increased formation of chlorates which play no part in bleaching. Furthermore, the cellulose, as well as the non-cellulose impurities in the wood pulp paste, was attacked. The material thus obtained was rich in oxy- and hydro-cellulose, as shown by its enhanced copper number. The α -cellulose content fell and the β - and γ -cellulose content rose. Although this is not important in paper-making, it is a disadvantage when the material is to be employed for making viscose and certain kinds of cellulose nitrate. This effect is observed only when chlorine bleaching agents are used, but not with ozone or hydrogen peroxide. In knot-pulp, the use of ultraviolet light in conjunction with hypochlorite bleaching did not exert a deleterious action, presumably because the chlorine reacts more readily with the ligneous constituents than with cellulose.

According to Edge and McKenzie,³⁷ light causes two changes in paper pulp, a yellowing and a fading or whitening. Sunlight causes a definite yellowing in three hours, and whitening only after about two weeks. The latter effect may be due to a bleaching of pulp constituents not removed in ordinary bleaching. Discoloration is more rapid at 90 per cent than at 30 per cent relative humidity, and is great for samples exposed to the sun's heat while shielded from its light. Yellowing by a mercury arc varies with the age of the lamp.

Wahlberg³⁸ believed illumination to effect a saving of bleaching liquor and of steam about equal to the cost of the light, but found application difficult because the light affects only the surface. Hirschkind, Pye and Thompson³⁹ obtain good results with a mercury arc, provided rays shorter than 3000A are removed since these are harmful to cellulose. Wave-lengths longer than 4000A are ineffective. The best range is 3500A⁴⁰ to 3850A.

Attempts at standardizing the test for the light-resistance of various fibrous paper-making materials have been made by Kovalevskii.⁴¹ An ordinary carbon arc produced after 80 to 100 hours changes in the resistance to breaking of paper and fiberboard that were too slight to be of use in the rapid laboratory testing of these substances. However, a Sperry carbon arc (150 amps., 79 volts, 950,000 c.p.) gave satisfactory results in exposures of twenty hours at 1.3 meters, in the case of sheets from unbleached sulfite pulp, sulfate kraft, straw pulp, mechanical wood pulp, linen rags, cotton, spruce, jute and a mixture of 60 per cent wool and 40 per cent kraft. All materials showed a decrease of 15 to 59.5 per cent in the resistance to breaking, with unbleached sulfite the most and jute and the two straw stocks the least affected. This contradicted a prevalent idea of the excessive destructibility of materials derived from lignified fibers. The stretching power of raw materials was impaired, but to a lesser degree than the resistance to breaking. Mechanical wood pulp and wool showed an increase in the stretching ability. The tests showed that in the process of aging by heat and light, all grades of paper undergo an insignificant change in their tearing length, and that this factor is less characteristic of the physical changes than is the resistance to breaking. The sorption of anthracene oil on raw materials was but little affected, except that that of wood pulp and wool was slightly improved.

The reflection of ultraviolet light by paper is not very different from that of

³⁷ Edge, S. R. H., and McKenzie, H. M., *Proc. Tech. Sect. Paper Makers' Assoc. Gr. Brit., Ireland*, 17, Pt. 2, 437 (1937); *Chem. Abs.*, 31, 4113 (1937); Bakker, H., *Chem. Weekblad*, 34, 543 (1937); *Chem. Abs.*, 32, 3958 (1938).

³⁸ Wahlberg, H. E., *Ind. Pappers Tid.*, 38, 481 (1934); *Chem. Abs.*, 28, 7008 (1934).

³⁹ Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, 105, TAPPI Sect. 268 (1937); *Brit. Chem. Abs.*, B, 147 (1938).

⁴⁰ Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, 105, No. 18, 118 (1937); *Chem. Abs.*, 32, 772 (1938).

⁴¹ Kovalevskii, I. I., *Bumazhnaya Prom.*, 14, No. 2, 13 (1935); *Chem. Abs.*, 29, 5264 (1935).

ordinary light.⁴² Papers water- and oil-proofed by vinyl resins are more readily penetrated by ultraviolet light than ordinary paper.⁴³ When paper containing resins is exposed to the sun, it tends to become yellow and soluble in cold weak alkalis or water.⁴⁴ The results may differ when artificial ultraviolet light sources are employed and these should be used only in the absence of sunlight. Bleached and unbleached rosin darkens in light,⁴⁵ and ferrous resinsates and rosin size, if contaminated with ferrous iron, are also light-sensitive. Ferric resinsates, aluminum resinate and sodium resinate have no ability to cause yellowing of paper in light.

Oguri,⁴⁶ in giving data on the increase in the copper number of filter paper, tissue paper and viscose rayons which follows exposure of these products to the rays of a quartz mercury arc, attributed it to the action of ozone formed by the lamp. Aldehydes appeared to be formed even in the absence of oxygen. Bromley⁴⁷ noted that when pulp-sized paper of good quality and free from resin is irradiated by the mercury arc, it rapidly loses its property of ink resistance, and the surface color degrades to a brown shade. He believed the browning to be a function of the gelatin present, which he found to be degraded to simpler products.

Most studies of the deterioration of paper by light have been made in sunlight. Richter⁴⁸ found that after 50 to 100 hours, the sacrifice in tear strength and tensile strength was in general slight in comparison with the loss in folding endurance, even though the fold strength of the sample tested had been originally greatly enhanced by the application of glue. Rosin- and starch-sized papers were at least as sensitive to loss in writing qualities as were glue-sized papers. The protective effect of glass was marked in the case of papers made from purified wood fiber and sulfite papers were partly protected, but newsprint deteriorated as rapidly under glass as when exposed directly. When purified wood fiber papers under glass in hydrogen were exposed to sunlight, there was apparently no degradation. Sulfite papers under these conditions showed a loss in fold strength, although the copper number did not increase. When similar papers were exposed under glass with oxygen, they retained 78 and 38 per cent, respectively, of their original fold strengths. Changes in the copper number were in the same order. When air was substituted for oxygen, the fold strength retentions were 90 and 58 per cent, respectively. Neutral mineral oil coatings did not protect papers from oxidation in sunlight. A glycerolated paper was somewhat less sensitive. Surface sizing with various waxes and starch caused no improvement and rosin was definitely harmful. A coating of regenerated cellulose, prepared by means of properly applied viscose solutions, was advantageous both for fold strength and for fold retention. Sodium stannate appeared to have a protective action but deterioration was hastened by the presence of sodium molybdate or of iron compounds, at least in a water-leaf purified wood-fiber sheet. Water-leaf papers lose from one to two per cent in weight when exposed a hundred hours on each side. In wood veneer strips, the changes in copper number are very great and in the case of poplar wood a marked delignification takes place.

⁴² Dérivé, M., *Papier*, **38**, 1083 (1935); *Chem. Abs.*, **30**, 2379 (1936).

⁴³ Ohl, F., *Wochl. Papier-Fabr.*, **67**, 5 (1936); *Chem. Abs.*, **30**, 2755 (1936); see also Chinchin, I., *Bumashnia Prom.*, No. 12 (1924); **14**, 12 (1935).

⁴⁴ Marini, M., *Bol. stas. sper. Carta*, **6**, 16 (1927); *Chem. Abs.*, **21**, 2188 (1927).

⁴⁵ Kimberly, A. E., and Hicks, J. F. G., *Bureau Standards J. Research*, **6**, 819 (1931).

⁴⁶ Oguri, S., *J. Soc. Chem. Ind. Japan*, **37**, 620B (1934); *Chem. Abs.*, **29**, 1241 (1935); for the effects of various surrounding oxygen concentrations, see Oguri, S., and Yamaguchi, T., *J. Soc. Chem. Ind. Japan*, **40**, 300B (1937). Oguri, S., and Takei, M., [*J. Soc. Chem. Ind.*, **41**, 3 (1938)] find only wave-lengths less than about 3640A effective.

⁴⁷ Bromley, H. A., *Analyst*, **58**, 29 (1933).

⁴⁸ Richter, G. A., *Ind. Eng. Chem.*, **27**, 177, 432 (1935).

Red, green, lemon-yellow, dark brown-yellow and light brown-yellow window glasses each afforded some protection when papers (double-sized rag, rosin-sized papers from 50 per cent rag and 50 per cent sulfite pulp and pure sulfite paper) were exposed to direct sunlight for 523 hours or to diffused sunlight for 767 hours. The degree of protection depended upon the extent to which the filters removed the shorter wave-lengths, the range between 4600 and 4000A being strongly injurious. The yellow, green, and red glasses afforded practically the same protection.⁴⁹ The brown-yellow glasses gave the least protection, since both of them transmitted some wave-lengths down to about 3300A.

Blaisdell and Minor⁵⁰ studied the aging properties of a very white facial tissue made of highly bleached wood fiber and of a cream-colored toweling of under-bleached sulfite wood fiber, by determining the copper number and absorbent properties before and after exposure for one hour to a Victor ultraviolet lamp at a distance of ten inches at 38°C. The original copper numbers of papers of this type gave no clue as to their permanence. A large change in this test may be considered as indicative of a rapid loss of absorbent properties on normal aging.

A method advocated by Wright⁵¹ for waterproofing paper consists in impregnating it with a solution of gelatin, casein, or similar protein, and bichromate of potassium or sodium. On exposure to the rays of a quartz mercury arc, the protein becomes insoluble and the paper is strengthened and made waterproof. The solution may also be added to paper pulp and the irradiation carried out after sheeting.

Ruderman⁵² coats paper with a suspension of dry starch and sulfur in cold water and then exposes it to ultraviolet light.

Considerable application has been made of fluorescence in filtered ultraviolet light in the analysis of papers and paper-making materials but the discussion of this topic lies beyond the scope of this book.⁵³ Testi⁵⁴ states that with rays of 3000 to 4000A, sulfite cellulose yields a color not caused by lignin, sulfur or lignosulfurous materials, but by an unknown principle in wood and its bark which resists various chemical treatments. White papers containing cotton, linen and hemp fibers assume a light-yellow color, and paper from chemical cellulose a white color with slight yellow tinge, and paper prepared chiefly from mechanical wood pulp, an intense violet color.

In testing the water resistance of paper by a method of this type, Grant⁵⁵ grinds 100 gm. of icing sugar, dried at 100°C., in a mortar with 0.5 gm. of Rhodamine 6G and sprinkles it from a bottle through 70-mesh bronze gauze on the specimen (2 sq. in.) floated on distilled water at 21°C. The time is taken with a stop-watch until, in a dark room, the upper surface of the paper irradiated with filtered ultraviolet first exhibits a bright golden fluorescence. This means that the water has just penetrated the paper, causing solution of the dyestuff.

Artificial Silk. Grempe⁵⁶ states that in the weathering of rayon and silk fabrics, the destruction takes place on the surface exposed to the light. It is due to both water and the ultraviolet rays of the sun. These fabrics lasted for about half a year when exposed to the weather. Huczel⁵⁷ has given curves showing the effect of exposure to ultraviolet light on the strength of textile fabrics prepared

⁴⁹ Köhler, S., *Tek. Tid. Uppl. C Kemi*, **65**, 49 (1935); *Chem. Abs.*, **29**, 6379 (1935).

⁵⁰ Blaisdell, C. A., and Minor, J. E., *Paper Ind.*, **15**, 512 (1933); *Chem. Abs.*, **28**, 2525 (1934).

⁵¹ Wright, W. L., U. S. P. 1,542,539, June 16, 1925; *Brit. Chem. Abs.*, **B**, 627 (1925).

⁵² Ruderman, A., U. S. P. 1,723,581, Aug. 6, 1929; *Chem. Abs.*, **23**, 4573 (1929).

⁵³ For general discussions, see Dérivière, M., *Papier*, **38**, 637 (1935); *Chem. Abs.*, **29**, 7652 (1935); Grant, J., *World's Paper Trade Rev.*, **103**, 1463, 1506, 1508, 1550, 1588, 1666 (1935); *Chem. Abs.*, **29**, 5266 (1935); Lewis, S. J., *J. Soc. Chem. Ind.*, **41**, 99R (1922).

⁵⁴ Testi, G., *Raggi ultravioletti*, 297, 1926; *Chem. Abs.*, **22**, 1472 (1928).

⁵⁵ Grant, J., *J. Soc. Chem. Ind.*, **53**, 349T (1934); see also Noll, A., and Preiss, K., *Papier-Fabr.*, **35**, Tech. Tl., 213 (1937); *Chem. Abs.*, **31**, 7248 (1937).

⁵⁶ Grempe, P. M., *Kunst-Seide*, **9**, 462 (1927); *Chem. Abs.*, **22**, 2469 (1928).

⁵⁷ Huczel, P., *Rayon and Melland Textile Monthly*, **16**, 161 (1935); *Chem. Abs.*, **29**, 3170 (1935).

from viscose. The damage to viscose rayon is slightly greater in an atmosphere of 45 per cent relative humidity than in one of 65, or 90 per cent.⁵⁸ Acetate rayon deteriorates less than natural silk or other types of rayons.⁵⁹ Among various protective agents tested, β -methylumbelliferone and tannic acid were the most effective when test pieces were exposed to daylight through 3 mm. of ordinary window glass for 250 hours. Other protective agents, Tannigen FC, zinc salicylate and maleic acid, were found better when the acetate rayon was exposed to daylight through Uviol glass. Quercitin was best when the samples were exposed to the light of a mercury arc. The protective agents were used in 2 per cent solution, 1 per cent being usually taken up by the fiber. Eichler gave the following results for the deterioration of various products. The first number is the percentage decrease in tensile strength resulting from six hours of exposure to the mercury vapor lamp and the second that after exposure of 250 hours to daylight through window glass; natural silk, 28, 62; cupranmonium rayon, 11, 57; viscose rayon, 4, 35; acetate rayon, 35, 24; acetate rayon dyed black, 0, 1.2; acetate rayon dyed blue, 11, 17; acetate rayon dyed brown, 11, 13; unbleached cotton, 0, 0.

In the preparation of a selvage-resistant material, Malm and Fordyce⁶⁰ form a sheet containing an ester of cellulose having an unsaturated acyl group such as cellulose tricrotonate and polymerize it by intense ultraviolet light for about five hours, or heat it to 100°C. for at least 24 hours.

The solubility properties of organic derivatives of cellulose may be modified by treatment with ultraviolet rays in the absence of oxygen.⁶¹

Silk. The photochemical destruction of this fabric depends upon the pH at which the exposures are made.⁶² The maximum stability to the light of a glass-enclosed carbon arc is at about pH 10, the pH being measured in the aqueous extract of the sample. Above pH 11 and below pH 3, the stability decreases rapidly. In the intervening range, a minimum exists in the neutral region, indicating that the protein salts formed with small quantities of acid or alkali are more stable than the pure protein.

During the deterioration of silk in sunlight or north skylight, the ammonia nitrogen content is increased, as a result of oxygen attacking the silk under the influence of light.⁶³ Saito⁶⁴ found that exposure of silk fabrics to direct sunlight for 49 days gave a loss of 95.3 per cent of their tensile strengths. Against this, coatings of antioxidants had little effect.

X-ray diagrams of unweighted silk appeared similar before and after exposure to an S-1 sunlamp, but photometric analysis indicated a decrease in fiber orientation, causing the long fiber arc to expand toward the character of a powder pattern.⁶⁵ Lead-weighted silk underwent the greatest deterioration.⁶⁶ Pure-dye and 25 per cent tin-weighted samples slightly increased in tensile strength when

⁵⁸ Negishi, M., Umesawa, H., and Mori, H., *Rayon World*, 5, No. 7, 1 (1937); *Chem. Abs.*, 32, 4343 (1938).

⁵⁹ Eichler, A., *Melland Textilber.*, 16, 429 (1935); *Chem. Abs.*, 29, 7084 (1935).

⁶⁰ Malm, C. J., and Fordyce, C. R., U. S. P. 1,973,493, Nov. 9, 1934, to Eastman Kodak Co.; *Brit. Chem. Abs.*, B, 737 (1935).

⁶¹ Bincer, H., German P. 601,478, Aug. 16, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 28, 7527 (1934).

⁶² Harris, M., and Jessup, D. A., *Bureau Standards J. Res.*, 7, 1179 (1931); *Am. Dyestuff Reporter*, 20, 795; 23, 215 (1934). Cf. Triotman, S. R., *J. Soc. Chem. Ind.*, 55, 325T (1936).

⁶³ Harris, M., *Textile Mfg.*, 60, 420 (1934); *Chem. Abs.*, 29, 4589 (1935); *J. Bur. Stands. J. Res.*, 13, 151 (1934); *Am. Dyestuff Rept.*, 23, 215 (1934); *Chem. Abs.*, 28, 5675 (1934); Colombo, G., *Boll. ufficiale staz. sper. seta*, 4, 73 (1934); *Chem. Abs.*, 31, 8204 (1937).

⁶⁴ Saito, S., *J. Soc. Rubber Ind. Japan*, 7, 92 (1934); *Chem. Abs.*, 28, 3591 (1934).

⁶⁵ Bruner, E., and Goehring, M., *Textile Research*, 5, 231 (1935); *Chem. Abs.*, 29, 4948 (1935).

⁶⁶ Hess, K., and Bruner, E., *Kansas Agr. Expt. Sta. Rept.*, 120 (1934); *Chem. Abs.*, 30, 2765 (1936).

exposed to wave-lengths longer than 3400A, but 50 per cent tin-weighted silk showed little or no change under these rays. All samples showed the greatest deterioration when exposed to wave-lengths between 2600 and 3400A, or to the entire spectrum. In dyed silks, color fastness was not in general sufficient to withstand Kansas sunshine, although only one sample in thirteen faded by the Fade-Ometer test.⁶⁷

Sericin solutions are cleared and reduced in viscosity by ultraviolet light.⁶⁸

Wool. Exposed wool no longer gives the von Allwörden reaction.⁶⁹ Meunier and Rey⁷⁰ observed that neutral wool develops a rose-violet color when treated with the vapor or solution of quinone, but a deep brown if previously exposed to sunlight or ultraviolet rays, the wool becoming more acid. This sharp difference may be utilized for the production of photographic prints on woolen fabrics. The effect of the irradiation is not dependent upon the nature of the surrounding atmosphere.

The superficial erosion of woolen cloth exposed to the air is ascribed by Heermann to the action of ultraviolet rays (2000-3500A).⁷¹ After exposure to sunlight, wool swells strongly in dilute alkali and crumples in a characteristic manner.⁷² After such exposure, it is dyed more deeply by basic dyestuffs and less so by acid dyes. Those dyes which yielded darker shades on wool which had been affected by sunlight than on unexposed wool were called positive. Those which yielded lighter shades after exposure were called negative. The positive or negative behavior of a dye toward wool usually increased with the duration of the exposure of the wool, but after a direct exposure of about 300 hours which almost completely destroyed the epithelial scales of the wool, the effect diminished. Indigo is positive after the wool has been exposed 100 hours, but after 264 hours, it is strongly negative. The behavior of acid dyes on exposed wool varies according to the acidity or neutrality of the bath from which they are applied. Alizarin Cyanin Green G is negative when applied from a neutral bath or one containing 3 per cent of acetic acid, but is strongly positive when applied from a bath acidified with 2 per cent of sulfuric acid. The differences in the behavior of dyes toward exposed wool are very considerably diminished if the wool is chromed before dyeing. The intense yellow color of exposed wool dyed by immersion in a cold aqueous solution of methyl orange is not removed by washing with water. Under similar conditions the color is readily removed from non-exposed wool.

The interior of exposed wool is alkaline, since it gives a bluish-violet color with haematin. The outer part is acid and gives a yellow-brown color. After prolonged exposure to sunlight, the wool becomes brittle and the fibers may be easily broken. Exposed wool is much more easily wetted than unexposed wool.

Irradiated wool fails to give the usual colors when treated with ninhydrin or allantoin because of the presence of sulfur dioxide.⁷³ The increase in the content of labile sulfur is also shown by the reduction of nitro- compounds to amines. Insolation also increases the primary amino-groups as determined by the van Slyke method.

⁶⁷ For further data obtained by the light of the carbon arc, see Appel, W. D., and Jessup, D. A., *Proc. Am. Assoc. Textile Chem. Colorists*, 350, 354, 1935; *J. Research Bureau Standards*, 15, 601 (1935).

⁶⁸ Kaneko, H., *Bull. Chem. Soc. Japan*, 9, 409 (1934); *Chem. Abs.*, 29, 662 (1935).

⁶⁹ Von Allwörden, K., *J. Soc. Chem. Ind.*, 35, 416 (1916); Naumann, K., *Ibid.*, 36, 707 (1917).

⁷⁰ Meunier, L., and Rey, G., *Rev. gen. mat. col.*, 28, 66 (1924); *J. Soc. Chem. Ind.*, 1924B, 370. *Compt. rend.*, 183, 596 (1926).

⁷¹ Heermann, F., *Chem. Ztg.*, 48, 337 (1924).

⁷² von Bergen, W., *Textilber.*, 6, 745 (1925); 7, 451 (1926); *Chem. Abs.*, 20, 2251 (1926); *Brit. Chem. Abs.*, B, 740 (1926).

⁷³ Meunier, L., and Rey, G., *Compt. rend.*, 183, 596 (1926); *Cuir Tech.*, 16, 530 (1927); *Chem. Abs.*, 22, 1047 (1928).

From 3.7 to 5.0 per cent of the sulfur content of cleaned wool samples is lost during exposure for 80 to 100 hours to the light from a quartz lamp.⁷⁴ This loss is more than doubled if the irradiation is followed by treatment with 0.001*N* sodium hydroxide. Microscopic examination shows the scales to be raised up; some are completely removed. It was suggested that the scales possess a higher sulfur content than the cortex so that a decrease in the number of scales explains in part the loss of the sulfur on irradiation.

Castiglioni⁷⁵ suggests that the yellowing of wool by ultraviolet light probably depends on the occurrence of the Salkowsky reaction between the sulfuric acid formed by oxidation of the sulfur of the wool and the cholesterol of the wool fat. Degreased wool tends to turn gray instead of the yellow to brown which forms in untreated wool.

The strength of wool is lost on exposure to light, slowly at first, then more rapidly and finally slowly again when but little strength is left.⁷⁶ Washing after exposure increases the loss of strength and results in a loss of weight owing to breakage of tendered surface hairs and to the dissolution of degradation products. Exposure also diminishes the extensibility. The product of extensibility and breaking load, a measure of the work of rupture, thus falls more rapidly than the breaking load itself and is probably a better measure of the useful strength of the cloth. The development of acidity is roughly parallel to the loss of strength. The Pauly test, however, gives positive results after a short exposure and soon reaches a maximum. Exposed cloth wets more rapidly and shrinks more when washed, but it fuls more slowly and has a lower regain.

Pretreatment of the wool with sulfuric acid is said to retard, and with alkalis to hasten, the deleterious action of light.⁷⁷ Rimington⁷⁸ has noted that free sulfhydryl groups are absent from normal wool and appear only after the action of alkalis or of ultraviolet light.

Smith and Harris⁷⁹ find irradiation of purified wool by the Fade-Ometer up to 100 hours progressively reduces its cystine content (from 12.2 to 7.9 per cent), with corresponding increases in ammonia nitrogen (0.28 to 1.22 mg. per gm.), alkali-solubility (11.9 to 36.2 per cent), and sulfate sulfur (0.06 to 0.37 per cent). Nearly all the sulfate sulfur in exposed wool is in the form of free sulfuric acid. There is a linear relation between cystine content and alkali-solubility in exposed wool. The deterioration is greater in wool previously treated by acid than in alkali-treated wool. The sulfur content of untreated and of acid-treated wool decreases during irradiation. This suggests that in the early stages, hydrogen sulfide is formed by a decomposition of the S—S group of cystine,⁸⁰ so that some is lost as hydrogen sulfide. The remainder is oxidized to sulfuric acid. Irradiation produces a type of oxidation different from that due to hydrogen peroxide. In nitrogen, hydrogen sulfide is evolved, the rate being increased by the presence of water.⁸¹

⁷⁴ Barritt, J., and King, A. T., *J. Textile Inst.*, **20**, 151T (1929); *Brit. Chem. Abs.*, **B**, 846 (1929); see also Sommer, H., *Chem. Ztg.*, **51**, 777 (1927).

⁷⁵ Castiglioni, A., *Chim. e l'Ind.*, **17**, 82 (1935); *Brit. Chem. Abs.*, **B**, 540 (1935).

⁷⁶ Cunliffe, C. W., *J. Textile Inst.*, **27**, T25 (1936); *Chem. Abs.*, **30**, 3244 (1936).

⁷⁷ Sommer, H., *Chem. Ztg.*, **51**, 777 (1927). See, however, Smith and Harris.⁷⁹

⁷⁸ Rimington, C., *Biochem. J.*, **24**, 205 (1930).

⁷⁹ Smith, A., and Harris, M., *Am. Dyestuff Repr.*, **25**, 383P, 542P (1936); *Brit. Chem. Abs.*, **B**, 828 (1936); *J. Research Bureau Standards*, **17**, 97 (1936); *Rayon Textile Monthly*, **17**, 501, 727, 795 (1936).

⁸⁰ See also McMahon, P. R., and Speakman, J. P., *Trans. Faraday Soc.*, **33**, 844 (1937).

⁸¹ Harris, M., and Smith, A. L., *J. Research Bureau of Standards*, **20**, 563 (1938).

In order to ascertain the likelihood of oils staining textile fabrics, Gray⁸² proposes to expose pieces of tape, treated with the oil, to the light of a quartz mercury arc, using a standard oil for purposes of comparison. A half-hour exposure at a distance of six inches from the lamp was found sufficient to develop a stain with oils likely to discolor fabrics.

Paine, Radley and Rendell obtain fabrics fluorescent in ultraviolet light by impregnating them with an aminostilbenesulfonic acid.^{83, 84}

PHOTOCHEMISTRY OF DYES⁸⁵

Diazo-Compounds and Azo Dyes. According to Eggert and Schröter,⁸⁶ nitrogen is evolved at a constant rate during the photochemical decomposition of the diazo-compounds derived from 2-amino- α -naphthol-4-sulfonic acid and *p*-aminodiphenylamine. This diminishes gradually when the illumination is withdrawn. The quantum yield (about 0.35) is independent of the intensity and wave-length of the light and of the temperature and concentration of the diazo-solution. The same quantum yield is obtained when the solid compounds are studied. Schröter⁸⁷ also determined the rate of fading by comparison with color standards. The quantum yields so determined were somewhat higher, the deviations being considerable in the case of the product from *p*-aminodiphenylamine. The lower values found by measurement of the evolution of nitrogen are attributed to the occurrence of side reactions which inhibit the complete evolution of the liberated nitrogen. On adding acid, the yield is unchanged in the case of 2-amino- α -naphthol-4-sulfonic acid, but acid reduces that of the *p*-aminodiphenylamine compound from 0.52 to 0.35. Alkali reduced the quantum yield of the former to 0.15. With the latter, precipitation occurred. In alcohol solution, the yield is increased to 0.5 to 0.6 for both substances, possibly because of the formation of a soluble diazo-molecule-alcohol complex which favors the reaction.

Schmidt and Maier⁸⁸ concluded that the bleaching of 1,2,4-diazonaphtholsul-

⁸² Gray, T. T., *Oil Paint and Drug Reporter*, Aug. 9, 1915.

⁸³ Paine, C., Radley, J. A., and Rendell, L. P., U. S. P. 2,089,413, Aug. 10, 1937, *Chem. Abs.*, 31, 7264 (1937).

⁸⁴ For fluorescence tests applied to various textiles, see Derrett-Smith, D. A., *J. Textile Inst.*, 28, T145 (1937); *Chem. Abs.*, 31, 7256 (1937); Korda, P., and Dérèbère, M., *Tech. moderne*, 29, 355 (1937); Henk, H. J., *Kunststoffe und Zellwolle*, 19, 426 (1937); *Chem. Abs.*, 32, 3620 (1938); Radley, J. A., *Analyst*, 63, 266 (1938); *Chem. Abs.*, 32, 4344 (1938); Topholme, C. H. S., *Textile Colorist*, 60, 441 (1938); Radley, J. A., *J. Soc. Dyers Colourists*, 53, 376 (1937); Whittaker, C. M., *J. Soc. Dyers Colourists*, 53, 468 (1937); *Chem. Abs.*, 32, 1461 (1938). Undyed wool shows a weak violet fluorescence and undyed casein fiber a dead-white one. The results of ultraviolet-lamp readings should be considered as presumptive only, and should be rejected in the presence of contradictory evidence.

⁸⁵ For absorption data and a discussion of chromophore theories, see Brode, W. R., *Ber.*, 61B, 1722 (1928); *Bureau Standards J. Research*, 2, 501 (1929); *J. Am. Chem. Soc.*, 48, 1984 (1926); 51, 1204 (1929); Obreimov, I. V., and de Haas, W. J., *Proc. K. Akad. Wetensch. Amsterdam*, 32, 1324 (1929); Blumberger, J. S. P., *Chem. Weekblad*, 25, 282, 315 (1928); 29, 454 (1932); 30, 538 (1933); 32, 6, (1935); Hodgson, H. H., and Rosenberg, W., *J. Soc. Chem. Ind.*, 49, 405T (1930); Szegö, L., *Ber.*, 61B, 2087 (1928); 62B, 736 (1929); Cambi, L., and Szegö, L., *Ber.*, 61B, 2081 (1928); Funkhouser, J., and Brode, W., *J. Am. Chem. Soc.*, 56, 2172 (1934); Piper, J., and Brode, W., *J. Am. Chem. Soc.*, 57, 135 (1935); Chakravarti, G. C., *J. Indian Chem. Soc.*, 8, 503 (1931); Mangini, A., *Gazz. chim. ital.*, 65, 298, 308 (1935); Barkoff, S., *Bull. soc. chim.*, 2, 1288 (1935); Foster, D. G., *J. Am. Chem. Soc.*, 53, 654 (1931); Maki, T., *J. Soc. Chem. Ind. Japan*, 34, 496 (1931); Luszczak, A., and Grün, L., *Monatsh.*, 64, 349 (1934); Griffith, M. E., and Brode, W. R., *Ohio Agr. Expt. Sta., Bimonthly Bull.*, 192, 122 (1938); *Chem. Abs.*, 32, 7732 (1938); Lazarev, P., *Chimie et Industrie*, Special No., 457 (1928); Schumm, O., "Die spektrochemische Analyse natürlicher organischen Farbstoffe," Jena, Fischer; Zintl, E., and Rauch, A., *Ber.*, 58B, 234 (1925); Hirschler, L., *Biochem. Z.*, 190, 411 (1927); Szilard, A., *Ibid.*, 170, 185 (1926); Speas, W., *Phys. Rev.*, 31, 569 (1928); Merritt, E., *Ibid.*, 28, 684 (1926); Frideaux, E., *J. Soc. Chem. Ind.*, 45, 664, 678, 697 (1926); Dutt, S., *Quart. J. Indian Chem. Soc.*, 4, 99 (1927); Holmes, W., and Peterson, A., *J. Phys. Chem.*, 36, 633 (1932); Hewitt, J., *Sci. J. Roy. Coll. Sci.*, 3, 27 (1933); Scheibe, G., *Kolloid-Z.*, 82, 1 (1938); Scheibe, G., and Kandler, L., *Naturwiss.*, 26, 412 (1938); Sen-Gupta, S. B., *J. Indian Chem. Soc.*, 15, 263 (1938); *Chem. Abs.*, 32, 8939 (1938).

⁸⁶ Eggert, J., and Schröter, W., *Z. Elektrochem.*, 34, 602 (1928).

⁸⁷ Schröter, W., *Z. wiss. Phot.*, 28, 1 (1930); *Chem. Abs.*, 25, 43 (1931).

⁸⁸ Schmidt, J., and Maier, W., *Ber.*, 64B, 767, 778 (1931).

sonic acid (long used in the preparation of light-sensitive papers) in acid solutions exposed to direct sunlight, proceeds quantitatively with evolution of nitrogen and replacement of the diazo-group by a phenol radical. The reaction was conducted in acid solution so that the disturbing formation of azo dye in the bleached solution could not take place. Fukushima and Horio⁸⁹ find the reaction due to rays shorter than 4500Å, the photolysis being a reaction of zero order. It is not affected by change of temperature. The quantum yield was 0.16 at 3666Å. The addition of salts⁹⁰ had no effect on the order of the reaction.

Horio⁹¹ exposed papers treated with a series of diazo-compounds in a spectrograph to the mercury and tungsten arcs and found their spectral sensitivities to be simply related to their extinction coefficients, at least in the case of copying papers of 1-diazo- β -naphthol-4-sulfonic acid and of *p*-diazo-diphenylamine sulfate. In an extension of this work⁹² in which various diazo-compounds on paper were similarly exposed to an iron arc, and developed with suitable azo-compounds, it was found that some benzenediazonium compounds were decomposed at wave-lengths less than 4000Å, independently of the position of the substituent. The threshold values for light-sensitiveness coincide well with the limits of the molecular absorption.⁹³ Yamamoto⁹⁴ determined the effect of sunlight upon the rate of decomposition of α -naphthalene diazonium chloride. The velocity constant became twenty times greater in clear weather, 2.7 to 11 times greater when there was slight cloudiness, and was not increased in completely cloudy weather.

Crystal Scarlet is visibly oxidized and reduced when no special depolarizer is used in the presence of zinc oxide as photosensitizer.⁹⁵

Ultraviolet light causes a gradual fading of 0.005 per cent Congo red, the reaction not being due to ozone.⁹⁶

The photochemical reduction of methyl red in methanol by phenylhydrazine with chlorophyll solution as a photosensitizer by the wave-length 4358Å is zero molecular in order, according to Ghosh and Sen-Gupta.⁹⁷ Its velocity is independent of the phenylhydrazine concentration and of temperature (25 to 35°C.) and reaches a maximum at a 5×10^{-5} molar concentration of chlorophyll. The quantum efficiency is 0.45 when only the radiation absorbed by the chlorophyll is considered. The dark reaction is extremely slow. In benzene, however, the reaction is unimolecular with a constant proportional to the phenylhydrazine concentration and a quantum yield of 0.05. For the wave-length 5460Å, the reaction in both methanol and benzene is zero-molecular with a velocity independent of the phenylhydrazine concentration. The quantum yield varies between 1.0 and 0.1, decreasing with increasing chlorophyll concentration. If phenylhydrazine hydrochloride is used, the dark reaction has a measurable speed, independent of the chlorophyll concentration. The light reaction has a very low quantum yield and

⁸⁹ Fukushima, I., and Horio, M., *J. Soc. Chem. Ind. Japan*, **34**, 372, 374 (1931); *Chem. Abs.*, **26**, 2377 (1932); *Mem. Coll. Eng. Kyoto Imp. Univ.*, **6**, 179 (1931); *Chem. Abs.*, **25**, 4797 (1931).

⁹⁰ Kogan, N. M., Pischulina, A. F., and Ankinovich, A. G., *Anilino-krasochernaya Prom.*, **2**, No. 11, 34 (1932); *Chem. Abs.*, **27**, 5321 (1933).

⁹¹ Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934).

⁹² Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 322 (1934); *Chem. Abs.*, **28**, 6637 (1934).

⁹³ The results have also been extended to solutions containing, in addition to the diazo-compound, varying amounts of Crystal Scarlet 6RA Extra and of Orange II. Horio, M., and Yamashita, S., *Z. wiss. Phot.*, **33**, 273 (1935); *Brit. Chem. Abs.*, **A**, 713 (1935).

⁹⁴ Yamamoto, E., *J. Soc. Chem. Ind. Japan*, **38**, 275B (1935); *Chem. Abs.*, **29**, 6492 (1935).

⁹⁵ Fukushima, I., Horio, M., and Ohmori, M., *J. Soc. Chem. Ind. Japan*, **35**, 398B (1932); *Chem. Abs.*, **26**, 5848 (1932).

⁹⁶ Puchkovskii, B. S., and Nekudov, V. N., *Kolloid-Z.*, **66**, 191 (1934); *Chem. Abs.*, **28**, 2623 (1934).

⁹⁷ Ghosh, J. C., and Sen-Gupta, S. B., *J. Indian Chem. Soc.*, **11**, 65 (1934); *Chem. Abs.*, **28**, 3662 (1934).

small temperature coefficient. Its unimolecular constant is proportional to the concentration of the reducing salt. An activated complex of chlorophyll and methyl red is believed to play a part in the reaction mechanism.

Since the photolytic oxidation of cellulose is accompanied by the evolution of carbon dioxide and since cotton dyed with simple azo-dyes yields more carbon dioxide upon irradiation than undyed cotton, Haller and Ziersch⁹⁸ conclude the dye fading to be an oxidative process. The carbon dioxide production is greater when the samples are exposed in an atmosphere rich in oxygen.

Exposure of a dilute (1:10,000) aqueous solution of 1-*p*-sulfobenzeneazo-N-phenyl- β -naphthylamine to sunlight gives *ang.* naphtho-phenazine and mainly the betaine of 3-phenyl-2-*p*-sulfophenyl- $\alpha\beta$ -naphth-1,2,3-triazolium hydroxide.⁹⁹ Exposure of 1-benzeneazo-N-phenyl- β -naphthylamine on cotton immersed in water gives after concentration of the extract and treatment with picric acid, 2,3-diphenyl- $\alpha\beta$ -naphth-1,2,3-triazolium picrate, but not *ang.* naphtho-phenazine. The N-benzyl derivative of 1-benzeneazo-N-phenyl- β -naphthylamine is much more stable to light. Diphenyl-4,4-*bis*-(8-azo-N-phenyl- β -naphthylamine) on cotton is bleached rapidly by sunlight in air or oxygen. In nitrogen, bleaching is very slow. Azo-dyes from N-alkyl- β -naphthylamines are not so readily convertible into triazolium salts and are much more stable in light.

Golden yellow solutions of $(C_6H_5)_3CN=NC_6H_5$ are decolorized rapidly when exposed to light of short wave-lengths.¹⁰⁰

Triphenylmethyl and Triphenylmethane Dyes. The free radical, triphenylmethyl, was found by Gomberg and Cone¹⁰¹ to be bleached in sunlight in benzene solution with the production of triphenylmethane and unidentified substances. Schmidlin and Garcia-Banús¹⁰² and, more recently, Bowden and Jones¹⁰³ found the products to be triphenylmethane and diphenyl-*bis*-diphenylenethane. The process occurs slowly in diffused light. Visible light (5300-4000Å) is the most active portion of the spectrum. The presence of triphenyl peroxide or triphenylchloromethane does not alter the reaction, but the nature of the solvent has a marked effect on the rate of the reaction. In toluene, decolorization was more rapid than in benzene; in 1,3,5-trimethylbenzene and *m*-xylene it was even faster, and in hexane, the most rapid. No loss of color was observed in sulfur dioxide solutions and in the solid state the photochemical change was of a low order.

Triphenylmethyl peroxide has been obtained in 45 per cent yield by exposing a cyclohexane solution of triphenylbromomethane with air or oxygen for eight days to light (less than 3800Å) from a Pyrex mercury arc.¹⁰⁴ It is highly probable that triphenylmethyl and bromine are formed by primary dissociation.

According to Tănăsescu,¹⁰⁵ 2,4-dinitrotriphenylmethane on insolation in neutral solutions yields the red O-quinone derivative, and in pyridine, the green nitrosocarbinol. In sunlight, 5-chloro-2-nitro-4',4''-diaminotriphenylmethane gives¹⁰⁶ a blue compound and a compound $C_{24}H_{20}O_2N_4Cl_2$, reduced by tin and hydrochloric acid to 2,4,4''-triaminotriphenylmethane. Similarly, 2-nitro-4',4''-diaminotriphenylmethane gives a blue compound and a compound $C_{24}H_{20}O_2N_4$. The diethylmercaptol of Michler's ketone¹⁰⁷ quickly turns green in light, especially when moist. A solution of triphenylmethane and triphenylchloromethane in light forms triphenylmethyl reversibly.¹⁰⁸

⁹⁸ Haller, R., and Ziersch, G., *Melliand Textilber.*, 10, 951 (1929); *Chem. Abs.*, 24, 3373 (1930).

⁹⁹ Krollpfeiffer, F., Mühlhausen, C., and Wolf, G., *Annalen*, 508, 39 (1933); see also Witt, O. N., *Ber.*, 20, 571 (1887).

¹⁰⁰ Lifschitz, I., *Ber.*, 58B, 2434 (1925).

¹⁰¹ Gomberg, M., and Cone, L. H., *Ber.*, 37, 3545 (1904).

¹⁰² Schmidlin, J., and Garcia-Banús, A., *Ber.*, 45, 1344 (1912).

¹⁰³ Bowden, S. T., and Jones, W. J., *J. Chem. Soc.*, 1149 (1928).

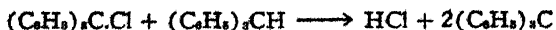
¹⁰⁴ Halford, J. O., and Anderson, L. C., *Proc. Nat. Acad. Sci.*, 19, 759 (1933).

¹⁰⁵ Tănăsescu, I., *Bull. soc. chim.*, 39, 1718 (1926); see also *Chem. Abs.*, 21, 533 (1927) for *o*-nitrotriphenylmethane.

¹⁰⁶ Tănăsescu, I., and Suciu, M., *Bull. soc. chim.*, 4, 245 (1937); *Brit. Chem. Abt.*, A II, 375 (1937).

¹⁰⁷ Madelung, W., *J. prakt. Chem.*, 114, 1 (1926).

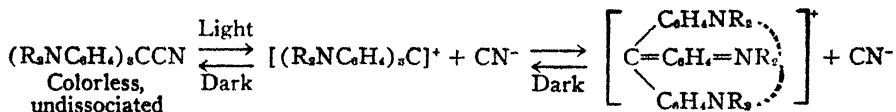
¹⁰⁸ Schlenk, W., and Herzenstein, A., *Ber.*, 43, 3545 (1910).



It has long been known¹⁰⁹ that the leucobases of triphenylmethane dyes (brilliant green, malachite green, crystal violet, etc.) are highly light-sensitive, readily producing the corresponding dyes. König¹¹⁰ made some attempts to utilize these photooxidations in color photography. Eder¹¹¹ believed that, mixed with collodion, the leucobases form films more light-sensitive than the dyed silver halide films previously used in the photometry of the visible region. Carroll¹¹² found these reactions to show no induction periods and to be proportional to the light intensity. The sensitivity was, however, too low for practical photographic application, although the oxidations may be accelerated by nitrogen bases, as heterocyclic and aliphatic amines.

Little use has been made of this behavior in actinometry. An important application of crystal violet and, particularly, malachite green in actinometry is, however, based upon a reaction of their leucocyanides, originally described by Lifschitz.¹¹³ It had been known that the addition of potassium cyanide to a triphenylmethane dye bleaches it with the production of a colorless triarylacetonitrile. Lifschitz showed that the colorless alcoholic solutions of the latter products were rapidly converted into the corresponding dyes when irradiated by an iron-nickel arc. The change occurred but slowly in sunlight in glass, so that it is due to the ultraviolet rays. When placed in darkness, the dyes again lose their colors. The leucocyanides in alcohol were not electrolytes. Irradiation was believed to convert them into colored, dissociated dye ions and cyanide ions, since the conductivity could be shown to increase. It was possible to demonstrate the liberation of the cyanide ion by setting up concentration cells of dark and illuminated solutions with silver cyanide coated electrodes.

Similar behavior was encountered in the thiocyanates and sulfonates of the triphenylmethane dyes, as well as in the dihydroxy-derivatives (benzaurin) and in unsubstituted triphenylmethyl cyanide. It became apparent that triphenylmethane derivatives can exist both in non-electrolyte and electrolyte forms. The primary photochemical effect was believed to consist in the transfer of a valence electron from the carbon atom to the cyanide or other group, which thereby becomes an ion. The triphenylmethyl ion need not, however, be colored until after it has undergone a further constitutional alteration. Lifschitz represented the process as follows:



Harris, Kaminsky and Simard,¹¹⁴ who studied the absorption spectra of the leucocyanides and products of photolysis of malachite green, found the Lifschitz mechanism inadequate to account for the phenomenon of fading of the color. They found the addition of water to the alcoholic (95-per cent) solutions to increase the rate of fading, which could be similarly accelerated by potassium hydroxide or

¹⁰⁹ Gros, O., *Z. physik. Chem.*, **37**, 157 (1901).

¹¹⁰ König, E., *Z. Angew. Chem.*, **17**, 1633 (1904).

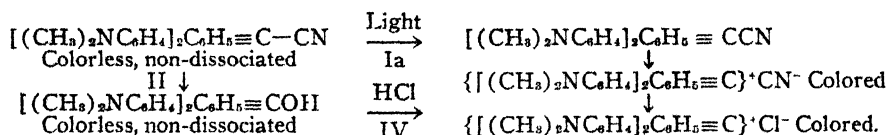
¹¹¹ Eder, J. M., *Phot. Korrr.*, **56**, 140 (1919); *Chem. Zentr.*, **90**, 396 (1919); *J. Soc. Chem. Ind.*, **38**, 878 (1919).

¹¹² Carroll, B. H., *J. Phys. Chem.*, **30**, 130 (1926).

¹¹³ Lifschitz, I., *Ber.*, **52**, 1919 (1919); **58B**, 2434 (1925); Lifschitz, I., and Joffe, C., *Z. physik. Chem.*, **97**, 426 (1921).

¹¹⁴ Harris, L., Kaminsky, J., and Simard, R., *J. Am. Chem. Soc.*, **57**, 1151 (1935).

cyanide. No dark reaction could be observed if hydrochloric acid was added either before or after the photochemical production of the color. The addition of the acid to partly faded solutions restored the color completely, unless the water content of the solutions exceeded 20 per cent, in which case there was only a 95 to 97 per cent restoration of the color. No color appeared when hydrochloric acid was added to a non-irradiated leuco-cyanide solution. This indicated that the product of the dark reaction in 95-per cent alcohol is not the original leucocyanide. In their modified mechanism, importance was attached to hydrolysis of the photo-compound. In the absence of hydrochloric acid, the final product of the dark reaction was assumed to be the colorless carbinol and not the original leucocyanide. Accordingly, they proposed the following scheme:



The carbinol can undergo a photolysis to the colored compound, which accounts for the regeneration by light of the partly decolorized solution. It was assumed that reaction I is instantaneous, but that reaction III may be slow or moderate. Reaction IV was known to be comparatively slow from measurements made with the pure carbinol. Reactions II and IV were found to be fast if hydrochloric acid was used during the photolysis. No evidence could be found for the formation of an intermediate compound in Ia. The dark reaction had a positive temperature coefficient. Ariga¹¹⁵ observed also that the colorless solution of malachite green produced by the action of alkali rather than cyanide (probably a colorless pseudo-ammonium base) regains its color when irradiated by a mercury arc or intense sunlight. The unimolecular rate constant was independent of the alkali concentration and temperature, but was proportional to the light intensity.

The Lifschitz reaction was made the basis of a useful actinometric solution by Weyde and Frankenburger,¹¹⁶ who used a pure alcoholic solution of the leucocyanide of crystal violet. The quantum yield of the color formation is unity for the wave-lengths 2537 and 3130Å. If enough cyanide was added to insure reversal in darkness, the solution was found to be suitable for use by physicians and meteorologists for measuring the erythema-producing rays of sunlight or artificial sources. In the case of this dye, the reverse dark reaction has a temperature coefficient of five. Its rate is proportional to the dye concentration and is greatly diminished by the presence of a little water.

For a precision actinometer, Harris and Kaminsky¹¹⁷ found the malachite green leucocyanide to be superior, since it has thirty times the solubility of the crystal violet leucocyanide. It was especially suited for the region between 3340 and 2480Å. With malachite green, a shorter cell-length may be used with certainty of 99.9-per cent absorption, the correction for inner-filter action by the photocompound is less, and colorimetric measurements can be made more accurately for the green dye. The quantum yield is unity.

Relatively little is known of the bleaching of the triphenylmethane dyes.

¹¹⁵ Ariga, T., *Bull. Chem. Soc. Japan*, **2**, 65 (1927); *Chem. Abs.*, **21**, 2103 (1927).

¹¹⁶ Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1931); Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).

¹¹⁷ Harris, L., and Kaminsky, J., *J. Am. Chem. Soc.*, **57**, 1154 (1935).

Henriquez¹¹⁸ believed that exposure of aqueous crystal violet solutions for several days converts it into a red dye, assumed to be fuchsine, by a replacement of the methyl groups by hydrogen. The presence of a free amino-group could be proved by diazotation and coupling reactions. Under similar conditions, malachite green was believed to be converted into Doebner's violet. With visible light, these color changes were more rapid than the bleaching of the dyes, but ultraviolet light destroys the colors, the more rapidly the more basic the solution. The oxidation of fuchsine by hydrogen peroxide is also brought about by ultraviolet light, the amino-groups being unaffected. Iwamoto¹¹⁹ states that in the presence of air and light, malachite green oxalate and crystal violet oxalate are converted into *p*-dimethylaminoacetophenone and Michler's ketone, respectively. In a sealed tube, the crystal violet oxalate gives the leuco- compound. Weyde, Frankenburger and Zimmermann¹²⁰ found that on prolonged irradiation of alcoholic solution containing potassium cyanide, the leucocyanide is completely destroyed, probably by oxidation.

Phthalein Dyes. The radiation of an arc light has been said to increase the rapidity of the oxidation of phenolphthalein to phenolphthalein.¹²¹

Fluorescein in glycerol solution exhibits a blue rather than a green fluorescence when irradiated by ultraviolet light. This is gradually and permanently lost on prolonged irradiation by wave-lengths shorter than 2540Å. Glycerol solutions of methylene violet, corallin, crocein, esculin, erythrosin, eosin and rhodamine similarly lose their fluorescent properties on exposure to ultraviolet light. Solutions of erythrosine, eosin and rhodamine in benzyl alcohol are much more sensitive to the action of light than are the glycerol solutions.¹²²

It has been suggested¹²³ that the bleaching of fluorescein dyes by light is a process of oxidation by hydrogen peroxide probably formed from water and oxygen, this reaction requiring an activation of the dye molecule by light.

Reychler¹²⁴ found no iodine liberated in darkness from solutions containing 0.125 gm. potassium iodide, 0.5 gm. of potassium dichromate and 0.01 gm. of eosin per 100 cc. in three hours. In weak diffused light after forty minutes the iodine liberated was equivalent to 2.8 cc. of 1-per cent sodium thiosulfate solution. After two and ten minutes in sunlight, the amounts of thiosulfate used were 6.3 and 16.4 cc.

In the presence of reducing agents, eosin is not hydrogenated¹²⁵ in darkness, even in warming. In sunlight or the light of a quartz lamp, it is almost instantly hydrogenated. The color returns quickly in darkness unless the irradiation has been unnecessarily prolonged, in which case the eosin is irreversibly changed into a strongly fluorescing substance.

Methylene Blue. Nurnberger and Arnow¹²⁶ find that aqueous solutions of methylene blue have two regions of absorption with maxima at 2920 and 2460Å. Irradiation of the solution with a mercury arc causes a decrease in the absorption in the visible and ultraviolet, the effect being greatest in the solutions of highest pH. The wave-lengths most active in decreasing the absorption are shorter

¹¹⁸ Henriquez, P. C., *Rec. trav. chim.*, **52**, 991 (1933).

¹¹⁹ Iwamoto, K., *Bull. Chem. Soc. Japan*, **10**, 420 (1935); *Brit. Chem. Abs.*, **B**, 1090 (1935).

¹²⁰ Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).

¹²¹ Rossi, G., *Chem. Zentr.*, **82**, 1659 (1911); *Giorn. Farm. Chem.*, **60**, 433 (1911).

¹²² Asterblum, M., *Bull. Intern. Acad. Polonaise*, **A7-B**, 297 (1924); *Chem. Abs.*, **20**, 1562 (1926).

¹²³ Blum, H. F., and Speelman, C. R., *J. Phys. Chem.*, **37**, 1123 (1933); see also Chakravarti, D. N., and Dhar, N. R., *Z. anorg. Chem.*, **142**, 299 (1925).

¹²⁴ Reychler, A., *Bull. soc. chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 544 (1926).

¹²⁵ Kögel, G., and Steigmann, A., *Phot. Ind.*, 1169 (1925); *Chem. Abs.*, **20**, 1035 (1926).

¹²⁶ Nurnberger, C., and Arnow, L., *J. Phys. Chem.*, **38**, 71 (1934).

than 2700Å. For this reason, the change in absorption by aqueous solutions of methylene blue cannot be used as a measure of the light intensity in the physiologically active region between 2900 and 3100Å.

Most photochemical studies on this dye have been concerned with coupled or sensitized processes. Brandt¹²⁷ studied the iron-sensitized reduction in the presence of ethanol and a phosphate buffer at pH 8.6. A considerable dark reaction occurred only when both alcohol and ferrous ions were present, and it was in such solutions that the greatest photosensitization was observed. The reduced solutions were reoxidized in the dark, an equilibrium being established which is displaced toward the side of leuco-methylene blue.

In light, zinc oxide acts on aqueous solutions of organic dyes of widely different classes.¹²⁸ In pure, air-free aqueous solution, the dyes are both oxidized and reduced. In the presence of an anodic depolarizer, they are exclusively reduced. With vat dyes, photolysis still occurs even at the highest reduction potentials, 0.15 v. in the case of safranin. A considerable difference in potential between the anodic and cathodic processes can be overcome by light. With azo-dyes, the photolytic reduction is not reversible, the products not reforming dyes on exposure to the air. Under certain conditions, sensitizing dyes can act upon other dyes as does zinc oxide. The necessary condition is that the absorption region of the sensitizing dye must coincide with that of the acceptor on the short wave-length side.

In the presence of zinc oxide as photosensitizer, Arro¹²⁹ found no vat dye formed during the bleaching of methylene blue. But in the presence of an anodic depolarizer (dextrose), the velocity of fading is increased and some vat dye is formed. The sensitizing action of yellow mercuric oxide is greater, and that of cadmium oxide, yellow lead oxide and the uranyl ion, less than that of zinc oxide. The addition of manganese dioxide, uranium dioxide or cadmium oxide increases the action of zinc oxide. The bleaching is irreversible.

Pyruvic acid, "Kojic" acid, ethyl acetoacetate, phloroglucinol and resorcinol reduce the dye in the absence of oxygen when irradiated.¹³⁰

The enzymatic reduction of the dye by *Bacterium pasteurianum* and by liver extracts is also speeded up by light. The dye molecule and not the hydrogen donor or the dehydrase is activated in the photochemical reaction.

The equilibrium potential of the methylene blue and phenylhydrazine sulfonate reaction is light-sensitive,¹³¹ the direction of the displacement of the equilibrium being opposite in light from the two ends of the visible spectrum. Hellström¹³² has observed that the redox potential of the methylene blue-ferrous ion system decreases reversibly in light, the potential change being dependent on the pH. However, the potential of the iron-free 50-per cent reduced dye is not affected by light, and the addition of ferrocyanide does not make it photosensitive. Light activation of the dye may cause the formation of a methylene blue-iron complex.

A procedure advocated by Marie and Raleigh¹³³ for the treatment of methylene blue for use in biological stains consists in dissolving one gram in 100 cc. of aqueous 0.5-per

¹²⁷ Brandt, K. M., *Arkiv Kemi, Mineral Geol.*, 12B, No. 7 (1935); *Chem. Abs.*, 30, 386 (1936); see also Weiss, J., *Trans. Faraday Soc.*, 32, 1331 (1936).

¹²⁸ Neuweiler, C., *Z. wiss. Phot.*, 25, 187 (1928); *Brit. Chem. Abs.*, 1928A, 457.

¹²⁹ Arro, H., *Commentationes Univ. Tartu A18*, (5) 3 (1930); *Chem. Abs.*, 26, 4255 (1932).

¹³⁰ Tamiya, H., Hida, T., and Tanaka, K., *Acta Phytochim.*, 5, 119 (1930); *Chem. Abs.*, 25, 1531 (1931).

¹³¹ Holst, G., *Z. physik. Chem.*, A175, 99 (1935); 179A, 172 (1937); *Nature*, 139, 285 (1937).

¹³² Hellström, H., *Naturwiss.*, 24, 76, 217 (1936).

¹³³ Marie, S. V., and Raleigh, J. T., *J. Lab. Clin. Med.*, 10, 250 (1924).

cent sodium bicarbonate solution and exposing in an open shallow dish to an arc lamp for ten to thirty minutes. When cool, there is slowly added 500 cc. of 0.1-per cent yellowish eosin solution until the surface becomes purplish with a metallic luster and a fine black powder is formed on the surface. After filtering and air-drying 0.1 gram is dissolved in 60 cc. of acetone free from methanol.

Irradiation of methylene blue, thionine, or brilliant cresyl blue in acid ferrous sulfate with the visible light of a strong carbon arc produces bleaching or a change in color, due to the formation of leuco- dyes, which is irreversible if the ferric ion formed is precipitated by hydrolysis. In darkness, the process is completely reversible, the ferric ion being reduced by the leuco- dye.¹³⁴ In the absence of the dye the irradiation of a 0.5 molar solution of ferrous sulfate in sulfuric acid by a strong mercury arc produces hydrogen when oxygen is excluded.

The rate at which Lauth's violet is bleached in aqueous methanol solution in the presence of diethyl- β -allylthiocarbamide as acceptor rises rapidly toward a limiting value as the concentration of the latter is increased, and at the same time the temperature coefficient falls. Hydroquinone, pyrogallol, and phenol retard the bleaching and also reduce the fluorescence of sodium naphthionate, the relative efficiencies being similar in each case. The part played by these substances in both processes depends on the deactivation of activated molecules by collisions. At high concentrations, electrolytes either accelerate the bleaching somewhat or retard it but slightly, although with small concentrations of some salts, there is a pronounced retardation.¹³⁵

If a 0.001-per cent aqueous solution of Lauth's violet (thionine) containing a small amount of ferrous sulfate (0.0075 mole per liter) and 0.01 molar sulfuric acid is cooled to -10°C . and exposed to the light of a powerful arc light, the dye is bleached in one or two seconds by a reversible process. The higher the temperature and the weaker the light, the slower the reduction. Lauth's violet has a positive reduction potential, 0.045 v. Methylene blue, Nile blue, phenosafranine and neutral red, all of which have negative normal reduction potentials, do not behave in a similar manner. In the case of methylene blue, photoreduction occurs if the ferrous sulfate is replaced by potassium ferrocyanide, which has a more negative reduction potential. The phenomenon can be explained by supposing that the photoexcited molecule (Lauth's violet) has a more positive reduction potential than the unexcited molecule, and even more positive than that of the ferric-ferrous ion system. Therefore, a reaction can occur with the formation of leuco- base and ferric ion. The maximum of the absorption band of Lauth's violet at 6000A corresponds to an energy (47,370 cal. per mole) more than sufficient for the above change. Methylene blue has a more negative reduction potential than Lauth's violet and its absorption maximum lies at longer wave-lengths (6700A) so that the energy absorbed is insufficient for the reaction to occur.

Bleaching of Dyes. The rate of loss of color of indigocarmine in ammonium oxalate solution by atmospheric oxidation under the influence of violet light obeys the law of mass action for concentrations ranging between 1 per cent and one to twenty thousand.¹³⁶ Similarly, the oxidation of helianthine follows the law, even in the range of concentrations in which solutions exhibiting an appreciable fluorescence do not follow it.

¹³⁴ Weiss, J., *Nature*, **136**, 794 (1935). See, however, Weber,¹³⁷ Leuco methylene blue turns blue in the light and is decolorized by standing in the dark, according to Matiu, A. I., and Popescu, C., *Bull. soc. chim.*, **4**, 1230 (1937). This had been previously observed by W. M. Clark, *U. S. Public Health Reports*, **40**, No. 23, 1131-1201 (1925).

¹³⁵ Weber, K., *Z. physik. Chem.*, **15B**, 18 (1931); *Naturwiss.*, **23**, 849 (1935).

¹³⁶ Perrin, J., and Choucroun, N., *Compt. rend.*, **187**, 697 (1928).

An increase of temperature between 15 and 45°C. retards the photochemical decolorization of benzene solutions of cyanine and gallocyanine.¹³⁷

Aside from the detailed studies which have been made on the photochemistry of individual dyestuffs, there have been many observations of the bleaching of dyestuffs in general. Some have contributed essential data on the relative light-fastness of different classes of dyestuffs. Others have been more or less speculative but have in some instances at least brought forward stimulating suggestions as to the mechanisms concerned.¹³⁸

Steigmann¹³⁹ raises the question as to why certain dyes are light-fast despite the absorption of energy by their chromophores. He suggests that in certain cases there may be a preferential action on other light-sensitive groups present in the molecule which cause an "intra-molecular desensitization." For this he considers alizarin an example. In other dyes, certain other groups, or configurations may exert an inhibitory action, but in this case the nature of the transformations of the absorbed energy is obscure.

Although some workers have found light to convert certain dyes, particularly of the triphenylmethane series, into other dyes, Barat and Dutt¹⁴⁰ find that, in general, sunlight decomposes dyestuffs directly into colorless products. In other words, the net effect is practically the same as that of a gradual dilution of the dye solution until its color becomes invisible. Spectrophotometric studies of the bleaching of a number of dyes have been published by Alberts.¹⁴¹

Leiber¹⁴² studied the effect of daylight in altering the absorption spectra of films of dyed gelatin made by pouring 10 cc. of an 8-per cent solution of the dye over a 100 sq. cm. glass mold. The dyes fell into three classes: (1) Bleaching makes the dye density gradually decrease. (2) A region of strong absorption was decreased and a field of weak absorption was strengthened. (3) The absorption maximum was displaced to other wave-lengths. The latter two classes were not entirely distinct. The following dyes were not affected by exposure to sunlight for 28 days and are suitable for the preparation of photographic filters: Crystal Ponceau 6R, Orange II, Pyrazole Yellow, Rapid Filter Yellow, Naphthol Green, Toluidine Green and Toluidine Blue.

The change of conductance of collodion films colored by cyanine, pinaverdol and pinachrome was observed by an electrometric method by Zehdro¹⁴³ during illumination. The collodion itself is unaffected by white light. The conductivity of the film increases with the time of illumination and at first is proportional to the time, but on longer exposures, the increase becomes less rapid and the conductivity gradually reaches a constant value. After the illumination ceases, the conductivity gradually diminishes. Cyanine showed a maximum conductivity at around 6000Å, pinaverdol at about 5700Å and pinachrome a sharp maximum at about 5800Å. Irradiation of a solution of cyanine in benzene produced a decrease in its electrical resistance, which rose again when the illumination ceased. Illumination with monochromatic light had this effect only when its wave-length was in the absorption band of the solution. Kosche¹⁴⁴ finds Indigosol IBL darkens in light, probably because of oxidation. Not all indigosol dyes are light-sensitive.

¹³⁷ Zehdro, N., *J. chim. phys.*, **26**, 178 (1929); *Chem. Abs.*, **23**, 3166 (1929).

¹³⁸ Kögel, G., *Phot. Korrr*, **68**, 83 (1932); *Chem. Abs.*, **26**, 5507 (1932).

¹³⁹ Steigmann, A., *Z. wiss. Phot.*, **27**, 268 (1929); *Brit. Chem. Abs.*, **A**, 174 (1930).

¹⁴⁰ Barat, K., and Dutt, S., *Quart. J. Indian Chem. Soc.*, **4**, 265 (1927); *Chem. Abs.*, **21**, 3194 (1927).

¹⁴¹ Alberts, H., *Z. wiss. Phot.*, **33**, 234, 249 (1935).

¹⁴² Leiber, F., *Kolloid-Z.*, **50**, 68, 117 (1930).

¹⁴³ Zehdro, N., *J. chim. phys.*, **26**, 59, 117 (1929); *Chem. Abs.*, **24**, 1578 (1930).

¹⁴⁴ Kosche, S., *Kleppig's Textil-Z.*, **40**, 584 (1937); *Chem. Abs.*, **32**, 6465 (1938).

Crespi¹⁴⁵ found no parallelism between the action of solar and ultraviolet radiation in their effects on cotton dyes. Ozone formation played no part in the action of the latter radiation. Evidence in support of an oxidation mechanism has been advanced by several workers. Scharwin and Pakschwer¹⁴⁶ exposed methylene blue, crystal violet, Congo red and eosin on cotton or paper in glass tubes in which were sealed various gases, to the action of sunlight or the light of a mercury arc. The speed of bleaching decreased in various gases in the following order: oxygen, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, hydrogen, nitrogen. No bleaching was observed under nitrogen and generally none with hydrogen, although in the latter case, decided changes due to reduction sometimes occurred. In oxygen, nitric oxide and nitrous oxide, carbon dioxide could always be detected after the exposure to sunlight. The changes due to oxidation were irreversible. When the dye was absorbed in porous clay, the amount of carbon dioxide produced after four months in sunlight was much less than in cases in which cotton was the substrate.

It has recently been pointed out that in practice consideration must be given not so much to the effect of light on a dye as to its effect on the entire fiber-dye system. A single dye may also fade, but may be permanent when present in admixture with a more resistant dye.

An early theory of the bleaching mechanism due to Gebhardt¹⁴⁷ assumed the intermediate formation of an organic peroxide of the dye, but not of hydrogen peroxide. The earlier literature of the fading of dyes on cotton fabrics was reviewed by Cunliffe.¹⁴⁸

Plain calico and similar fabrics dyed with Brilliant Copper Blue, Chlorazol Sky Blue and Benzopurpurin 4B were found by Miss Hibbert¹⁴⁹ to have almost unchanged copper numbers after exposure to 669 hours of bright sunshine. Since complete destruction of the dyes occurred long before the copper number of the fabric reached 3.6, it was concluded that the fading of dyed cotton is not due to a reducing action of the cellulose under the influence of light, as had been previously assumed.¹⁵⁰ Certain dyes retard or accelerate the tendering of cotton. Cotton fabrics dyed with Duranthrene Yellow, Cibacron Yellow and Indigo, which had an original tensile strength of 48 lbs. had tensile strengths of 27, 16 and 22 lbs., respectively, after exposure for 120 hours in a Fade-Ometer. Isatin could be obtained in a pure state by extraction from calico which had been dyed with indigo and exposed to light.¹⁵¹ In cotton materials dyed with chrome green, chromium hydroxide had a marked protective effect against sunlight.

According to Seyewetz and Mounier,¹⁵² nitrated coloring matters turn brown under the action of light, which probably has a reducing action. The brown substance is insoluble in water and slightly soluble in alcohol, but too little could be isolated for its composition to be determined.

Cotton fabrics dyed with *o*-toluencazo- β -naphthol became covered with bright lustrous crystals after exposure for three minutes to the light from a Fade-

¹⁴⁵ Crespi, F., *Atti congresso naz. chim. pura applicata*, **2**, 833 (1926); *Chem. Abs.*, **22**, 3532 (1928).

¹⁴⁶ Scharwin, W., and Pakschwer, A., *Z. angew. Chem.*, **40**, 1008 (1927).

¹⁴⁷ Gebhardt, K., *Z. angew. Chem.*, **22**, 2484 (1910); **23**, 820 (1910); *J. Chem. Soc.*, **98**, 405 (1910).

¹⁴⁸ Cunliffe, P. W., *J. Textile Inst.*, **15**, 173; see also Ellis, G. H., *Chem. Age*, **13**, 470 (1925); Barker, S., and Hirst, H., *J. Textile Inst.*, **17**, 483T (1926).

¹⁴⁹ Hibbert, E., *J. Soc. Dyers Colourists*, **43**, 292 (1927); *Chem. Abs.*, **43**, 292 (1927); *Brit. Chem. Abs.*, **B**, 840 (1927).

¹⁵⁰ See Harrison, W., *Ber.*, **47**, 689 (1914).

¹⁵¹ See also Haller, R., Hackl, J., and Frankfurt, M., *Textilber.*, **9**, 415 (1928); *Brit. Chem. Abs.*, **B**, 479 (1928). In contrast to Indanthrene Yellow, the fading of indigo is a process of oxidation.

¹⁵² Seyewetz, A., and Mounier, D., *Compt. rend.*, **185**, 1279 (1927); *Bull. soc. chim.*, **43**, 648 (1928); *Chem. Abs.*, **22**, 916 (1928).

Ometer.¹⁵³ The crystals were shown capable of sublimation and when recrystallized from chloroform were obtained as crystals of a different character but the same melting point as that of *o*-tolueneazo- β -naphthol. A thin layer of the powdered compound sublimed to only a very small degree at 45°C., the temperature reached in the irradiation, and it was not possible to obtain crystals as in the case of the dyed fabric. The cotton fabric suffered a loss of color due to this sublimation in the Fade-Ometer, but it did not change in color or become dull as it does when exposed in sunlight. Sublimation effects were observed also with cotton dyed with *o*-tolueneazo- α -naphthol and with combinations of Naphthol AS-BO and AS-RL with Fast Orange G base, but no crystals were formed on the surface.

Curtis¹⁵⁴ states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury arc. Neither are they bleached by the addition of 3-per cent hydrogen peroxide until the mixture is rayed. It was possible to exclude ozone as a cause of the bleaching. Holmes¹⁵⁵ reports that solutions of magenta, malachite green, methyl violet and crystal violet which had been decolorized by sulfur dioxide develop their original colors when exposed to ultraviolet rays of wave-lengths shorter than 3300Å.

The photo-oxidation of many dyes by potassium dichromate was studied by Plotnikov.¹⁵⁶ Aqueous solutions of the following dyes were not affected: trypan blue, induline, dahlia, aniline green, malachite green, naphthol green, iodine green, nigrosin, trypan red, erythrosine, indigocarmine blue, gentian violet, Guinea green B and G, Brilliant Safranin, Aurantia, safranin, lithion carmine, carmine II, rose Bengal, Rhodamine B, Hofmann violet, methyl violet, crystal violet, cresyl fast violet. On the other hand, ethyl green, cyanin and naphthalene blue change very rapidly, both in light and darkness. Nile blue and cresyl blue 2BS are stable in darkness even on boiling, but in light change fairly quickly to bright red, fluorescent substances.

TESTS FOR THE LIGHT-FASTNESS OF DYES

The reproducible determination of the light-fastness of a dye or the relative light-fastnesses of a series of dyes requires the consideration of several factors. The distribution of the energy available at various wave-lengths in the light of the source employed for the test is of the utmost importance for the rapidity and reproducibility of the results. In some dyes, the absorption is predominantly in the visible; in others there are additional bands in the ultraviolet. Furthermore, the absorption spectrum and photochemical behavior of a dye in pure solution or in a collodion film may differ from that which it exhibits when applied to a fiber. In addition, the absorption of light by the fiber must be taken into account, since it may either lessen the amount of light available for the destruction of the dye-stuff or it may cause photochemical changes in the fiber which result in the production of products which may hasten or retard the fading of the dye. The intensities of the radiations at various wave-lengths in sunlight vary extremely with the location at which the tests are conducted, with the time of year and with the amount of cloudiness, dust, smoke, etc. Variations in temperature, humidity, and the presence of acid fumes, also complicate the results of sunlight fading tests. As a result, it is difficult to secure reproducible results in successive tests at a given station, and far more so to make the results at one station compare with those obtained at another geographical location. For these reasons, exhaustive studies have been made by a Subcommittee on Light-fastness of the American Association

¹⁵³ Hibbert, E., *J. Soc. Dyers Colourists*, **44**, 300 (1928); *Brit. Chem. Abs.*, **B**, 854 (1928).

¹⁵⁴ Curtis, H. A., *J. Am. Chem. Soc.*, **42**, 720 (1920); *J. Chem. Soc.*, **118**, 342 (1920).

¹⁵⁵ Holmes, E. O., Jr., *J. Am. Chem. Soc.*, **44**, 1002 (1922).

¹⁵⁶ Plotnikov, J., *Z. Elektrochem.*, **32**, 13 (1926).

of Textile Chemists and Colorists¹⁵⁷ to find a substitute for sunlight whose fading action will have speed, similarity to the action of the sun, and a capacity for exact reproduction at different times and places. Similar investigations have been undertaken in other countries.¹⁵⁸ Recent workers have tended to emphasize the unsuitability of most artificial sources for giving results directly comparable with those of actual sunlight fading, since the effects in the latter case are predominantly due to absorption of visible rays, whereas the artificial sources most frequently advocated usually produce either disproportionately large amounts of the longer ultraviolet radiations of sunlight or even radiations of wave-lengths shorter than those available in sunlight.¹⁵⁹ Accordingly much effort has recently been expended in improving the sunlight test. Hibbert¹⁶⁰ observed that certain colors dyed on cotton and Cellophane exhibited very different fading rates when exposed to sunlight or to ultraviolet rays. The larger the proportion of short ultraviolet rays in the source employed, the greater the attack on the cellulose. This produces reducing substances which may affect the dye. Harrison¹⁶¹ observed that in vacuum under a mercury arc, cellulose reduced flavanthrene and many direct colors, the cellulose being itself oxidized. In sunlight, however, the cellulose is less rapidly attacked, and this explains why direct colors fade much more slowly in sunlight. The direct colors are said not to fade in the absence of the fiber, and wool is not as powerful a reducing agent for them as is irradiated cellulose. On the other hand, Harrison found basic colors to fade usually by oxidation processes, although fading by reduction may occur under certain conditions. Thus it is apparent that the nature of the substrate, as well as the spectral energy distribution, is involved in determining the results of fading tests.

It has frequently been stated that deep shades are faster than pale shades. Barker, Hirst and Lambert¹⁶² stated that measurements of the proportional losses of the predominant color in worsted fabrics dyed to different depths of shade with each of fifteen acid, mordant, and direct dyes, produced by sunlight and by light from a Fade-Ometer showed that the loss of color during fading was independent of the depth of the shade. Since the total color loss is the same for all shades, it is a much higher percentage of the total color in the pale than in the deep shades. Recently, however, attention has been called to the existence of a possibility that dyes exhibit a maximum sensitivity to light when present on the fibers at a certain concentration called the "mean critical tone." Pinte¹⁶³ believes that all comparative tests should be made at the previously determined "mean critical tone," since the fastness of a color improves the further it is from this value, whether toward zero, or 100. It is approximately 55 per cent for yellows, 45 per cent for oranges, 40 per cent for reds, and 35 per cent for violets, blues and greens.

¹⁵⁷ Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 225, 1925; *Am. Dyestuff Rept.*, **14**, 58; *Chem. Abs.*, **18**, 906 (1924). For general discussion on light-fastness tests, see Jameson, C. W., *Am. Dyestuff Rept.*, **21**, 306 (1932); Goodings, A. C., *Am. Dyestuff Rept.*, **24**, 663 (1935); Pestalozzi, S., *Zellstoff und Papier*, **17**, 53 (1937); *Chem. Abs.*, **31**, 3283 (1937); Dérivière, M., *Tiba*, **13**, 173, 175, 259, 329, 331, 415, 417, 481, 547, 549, 607, 687 (1935); Schupp, E., *Monatsh. Seide, Kunstseide*, **41**, 441, 488 (1936); Ris, H., *Kleppzig's Textil-Z.*, **39**, 731 (1936); Rein, H., *Ibid.*, **39**, 732 (1936); Beil, A., *Angew. Chem.*, **49**, 905 (1936); Hirst, H. R., *J. Soc. Dyers Colourists*, **41**, 347 (1925); Merck, O., *Farben Ztg.*, **34**, 1117 (1929).

¹⁵⁸ Lantz, L. A., and others, *Fastness Committee, Society of Dyers and Colourists*, 52 pp., 1934; *Chem. Abs.*, **28**, 7538 (1934).

¹⁵⁹ Rein, H., *Angew. Chem.*, **47**, 157 (1934).

¹⁶⁰ Hibbert, E., *J. Soc. Dyers Colourists*, **48**, 251 (1932), (*Chem. Abs.*, **27**, 192 (1933)).

¹⁶¹ Harrison, W., *J. Soc. Dyers Colourists*, **28**, 225 (1912).

¹⁶² Barker, S. G., Hirst, H. R., and Lambert, P. N., *J. Soc. Dyers Colourists*, **43**, 264 (1927); *Chem. Abs.*, **21**, 3746 (1927).

¹⁶³ Pinte, J., *Chambre Commerce Roubaix Lab. recherches ind.*, No. **25**, 10 (1935); *Chimie et industrie*, **34**, 923; *Chem. Abs.*, **30**, 1234 (1936).

Humidity is also an important factor. Hedges¹⁶⁴ observed that the fading by a Hanovia mercury arc of wool patterns dyed with Ponceau RG, Acid Green G and Cyanin B under various conditions of humidity indicated an increased fading with increased humidity of the atmosphere surrounding the dyed patterns. The losses for these three dyes were for Ponceau RG at 52 and 100 per cent relative humidities, 1.5 and 4.9 per cent, for Acid Green G at 33 and 100 per cent, 11.2 and 21.7 per cent, and for Cyanin B, at 24 and 100 per cent, 23.8 and 41.0 per cent.

It is also important to agree upon the use of a definite method for determining the extent to which fading has occurred in a test. Many methods have been suggested. Gebhard¹⁶⁵ recorded the change of color, whether fading or change to another tint, by orthochromatic photography, using a light filter of the same color as the original dyeing. Appel and Smith¹⁶⁶ recorded the fading in the form of quantitative reflection measurements. Bravo¹⁶⁷ used a Pulfrich step photometer with that one of three spectral filters which most nearly coincided with the predominant color of the dye in making his observations. Mougeot¹⁶⁸ preferred a Toussaint photocolormeter and believed "etalons" unsatisfactory. Niederhauser¹⁶⁹ recommended the use of a photocolormeter and, in the exposure the Toussaint and Pinte "insolameter," which excludes dispersed daylight and measures the amount of light received by the illuminated materials. Probably the greater number of observers rely upon a simple visual comparison of the faded material with dyed patterns retained in darkness as standards. Hirst, in an earlier period,¹⁷⁰ indeed, considered such results as of more value than those obtained with the instruments then available.

Sunlight Tests. Much evidence has been accumulated as to the effects of variations of weather conditions on these tests; the data is so extensive that the original papers must be consulted. Barker and Hirst¹⁷¹ investigated the effects on patterns on worsteds dyed with Victoria Blue and 85 other dyes, of sunlight during the months January to June in Leeds and in the country nearby, and also under five different cloud conditions. Full sunlight caused a fairly constant relative fading of Victoria Blue. Dull light had about one-tenth the effect of full sunlight. With Wardle, they charted the comparative sunlight values for different hours of the day for the six months included.¹⁷² The value of the light for the total period of exposure could be expressed, by the aid of their graphs, in terms of what they considered a definite unit, one hour of June midday sun. For the variations of sunlight in the United States, and the differences between sunlight and the light of various artificial sources, see Anderson.¹⁷³

Cady¹⁷⁴ found the angle of exposure to be important, the fading being greatest

¹⁶⁴ Hedges, J. J., *J. Soc. Dyers Colourists*, **43**, 261 (1927); Hill, L., *Ibid.*, 296, Cunliffe, P. W., *Ibid.*, **45**, 215 (1929); *Chem. Abs.*, **21**, 3746 (1927); **23**, 4824 (1929).

¹⁶⁵ Gebhard, K., *Farben. Ztg.*, **22**, 6 (1911), various methods have been discussed by Cunliffe, P. W., *J. Soc. Dyers Colourists*, **45**, 215 (1929).

¹⁶⁶ Appel, W. D., and Smith, W. C., *Proc. Am. Assoc. Textile Chem. Colorists*, **180** (1928), *Chem. Abs.*, **22**, 3048 (1928).

¹⁶⁷ Bravo, G. A., *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, **8**, 50 (1930); *Chem. Abs.*, **24**, 2888 (1930); *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, **9**, 210 (1931); *Chem. Abs.*, **26**, 2321 (1932).

¹⁶⁸ Mougeot, P., *Bull. soc. franç. elec.*, **5**, 965 (1935); *Chem. Abs.*, **30**, 4676 (1936).

¹⁶⁹ Niederhauser, *Klepsig's Textil. Z.*, **39**, 739 (1936); *Chem. Abs.*, **31**, 1623 (1937).

¹⁷⁰ Hirst, H. R., *J. Soc. Dyers and Colourists*, **41**, 347 (1925); *Brit. Chem. Abs.*, **1926B**, 43.

¹⁷¹ Barker, S. G., and Hirst, H. R., *J. Textile Inst.*, **17**, 483T (1926); *J. Soc. Chem. Ind. Suppl* 976 (1926).

¹⁷² Barker, S. G., Hirst, H. R., and Wardle, G. C., *J. Soc. Dyers Colourists*, **43**, 324 (1927).

¹⁷³ Anderson, W. T., Jr., *Proc. Am. Assoc. Textile Chem. Colorists*, 273 (1928). Note also Appel, W. D., *Ibid.*, 275, and Cady, W. H., and Appel, W. D., *Ibid.*, 179 (1927).

¹⁷⁴ Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 225 (1925); *Chem. Abs.*, **20**, 668 (1926).

with horizontal exposures and less in order with 45° and with vertical ones. The angle of exposure is important only when total fading is considered; it has little effect on relative fading. Covering the samples with glass has effects which differ with different dyes. The effect of free circulation of air or the lack of it cannot be ignored. Continuous exposure produces different fading from that due to exposure only to the high cloudless sun. Direct sunlight has a different effect from skylight without sun. Exposures made in different localities show little variation in relative fading.

Barker and Hirst¹⁷⁵ described an exposure cabinet for protecting the patterns from dirt, soot and rain. As a transparent, protective screen they employed Vita glass (see Chapter 10). Cady and Appel¹⁷⁶ recorded the energy received by some of the samples with the aid of a barium photoelectric cell and automatic recorder. They found that approximately reproducible relative fadings could be obtained in a series of dyeings exposed in widely separated stations in the United States at different times in the year at an angle of 45° from the horizontal, facing south, between 9 A.M. and 3 P.M. on sunny days only, in a cabinet covered with a good grade of window glass approximately one-eighth inch thick. The cabinet was open at the sides and the distance between the glass and the samples not less than one-half inch. They felt that no artificial light source could be recommended. The quantity of radiant energy as recorded in some of the exposures did not correspond to the amount of fading produced. In later work embracing 1252 dyeings on cotton, wool, silk and weighted silk of 381 different coloring matters¹⁷⁷ they found the presence or absence of a glass cover to have a marked effect on the fading in only 4 per cent of the samples. Earlier observations by Pierce¹⁷⁸ had indicated that glass keeps out most of the active rays. Hirst¹⁷⁹ had suggested that dyes intended for outside purposes should be directly exposed to sun and weather and that those intended for inside indoor use should be exposed under glass. It would seem that the use of Vita glass would permit the fading of the small group of dyes not susceptible to the wave-lengths transmitted by glass without complicating the results in the case of other dyes by the use of radiations not present in the solar spectrum.¹⁸⁰ Appel and Smith¹⁸¹ tested Corex, Vita and six other glasses on twenty samples determining the extent to which the fading was affected by the manner in which they change the distribution of the intensities at various wave-lengths. It was found that the visible and long-wave ultraviolet of sunlight were relatively more important in comparison with the shorter wave-lengths of sunlight than had been commonly supposed. As a result they considered window glass satisfactory for the standard sunlight test.

Hirst,¹⁸² who favored the use of the usual five degrees of fastness selected as standards the following dyes, given in increasing order of fastness: 0.4 per cent Indigocarmine X (BDC). I. 1.5 per cent Ponceau RG (BDC). II. 2.75

¹⁷⁵ Barker, S. G. and Hirst, H. R., *J. Soc. Dyers Colourists*, **43**, 300 (1927); *Chem. Abs.*, **21**, 3747 (1927).

¹⁷⁶ Cady, W. H., and Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 179, 1927; *Chem. Abs.*, **22**, 319 (1928).

¹⁷⁷ Cady, W. H., and Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 217 (1929); *Am. Dyestuff Rept.*, **18**, 407; *Chem. Abs.*, **23**, 4824 (1929).

¹⁷⁸ Pierce, E. W., *Chem. Eng.*, 97 (1918); *Textile World J.*, Jan. 12, 1918.

¹⁷⁹ Hirst, H. R., *J. Soc. Dyers and Colourists*, **41**, 347 (1925); *Brit. Chem. Abs.*, **B**, 43 (1926).

¹⁸⁰ Griffith, I. O., and Jenkins, R. G., *J. Soc. Dyers Colourists*, **43**, 297 (1927) find plate glass as used in shop windows to transmit 90 to 95 per cent of the visible spectrum and a small proportion of the ultraviolet from 3500 to 3000 Å but scarcely any of that between 3000 and 2900 Å.

¹⁸¹ Appel, W. D., and Smith, W. C., *Proc. Am. Assoc. Textile Chem. Colorists*, 180 (1928); *Chem. Abs.*, **22**, 3048 (1928).

¹⁸² Hirst, H. R., *J. Soc. Dyers and Colourists*, **41**, 347 (1925); *Brit. Chem. Abs.*, **B**, 43 (1926).

per cent Azorubine (Sand.). III. 4.5 per cent Kiton Red S (CAC). IV. 2.5 per cent Chlorazol Fast Red FG (BDC). V. Indigo Full Shade or Natural Green B (C).¹⁸³ Tables of the German, English and American standards of dyes for light stability have recently been given by Wahl.¹⁸⁴ The standard wool dyes were tested at stations all over the world and were found to be of value in comparing the light effects available at various localities for testing other dyes simultaneously.

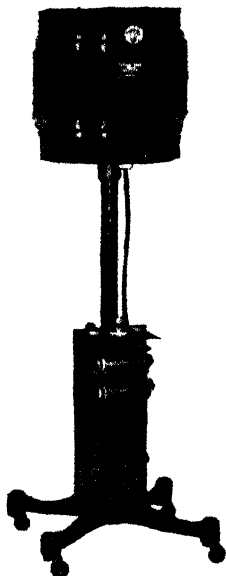


FIGURE 128.

Apparatus for Dye or Paint Testing.

Courtesy Cooper-Hewitt Electric Co.

Use of Artificial Sources. A number of early observers felt that the saving in time by and, they believed, greater reproducibility of the mercury arc as a source would more than compensate for any differences in fading which some dyes might exhibit under it.¹⁸⁵ Pierce believed that one hour under the mercury arc roughly paralleled an average day of exposure to sunlight. Apparatus of this type is commercially available (see Fig. 128) for both dye and paint testing. It consists merely of a circular cabinet about a vertical quartz mercury arc. The walls support removable panels to which the samples are attached. In comparing the action of the mercury arc with that of the sun, Scheurer,¹⁸⁶ who attempted to protect the dyes from any ozone formed, found that indigo resisted the mercury arc better than it did sunlight, although Benzo colors which were hardly faded by sunlight were materially changed by the mercury arc in 24 hours. After an extended study, Harrison¹⁸⁷

¹⁸³ Note also Deady, W. F., *Proc. Am. Assoc. Textile Chem. Colorists*, 242 (1925); Appel, W. D., *Am. Dyestuff Rep.*, 27, *Proc. Am. Assoc. Textile Chem. Colorists* P 15 (1938).

¹⁸⁴ Wahl, A., *Rev. gén. mat. color.*, 40, 140 (1936); 41, 460 (1937). See also Cunliffe, P. W., *J. Textile Inst.*, 28, 203 (1937). For a new blue fastness scale, see Müller, E., *Kleppig's Textil Z.*, 39, 732 (1936); Rein, H., *Angew. Chem.*, 47, 157 (1934). A standard should be adopted for interrelating fastness to light and to weather, according to Vendor, A., *Monatschr. Textil-Ind.*, 52, 262 (1937); *Chem. Abs.*, 32, 1458 (1938).

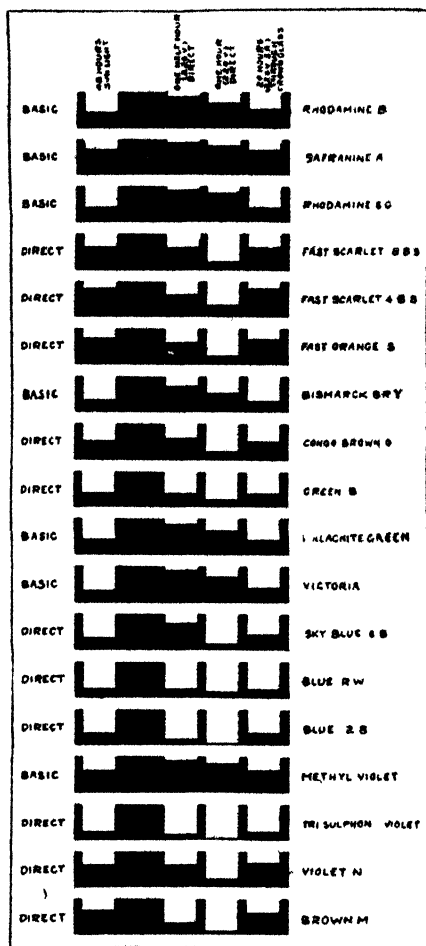
¹⁸⁵ Pierce, E. W., *Chem. Eng.*, 97, 1918; *Textile World J.*, Jan. 12, 1918; Flynn, O. R., *Am. Dyestuff Repr.*, 12, 837 (1923); Gebhard, K., *Farben Ztg.*, 22, 6 (1911).

¹⁸⁶ Scheurer, A., *Bull. soc. ind. Mulhouse*, 80, 324 (1911).

¹⁸⁷ Harrison, W., *J. Soc. Dyers and Colourists*, 28, 225 (1912).

agreed not only that there are differences between the sun and the mercury arc effects but also that the effects are different with mercury arcs of high and of low intensity. Flynn¹⁸⁸ extended these results and also used a filter of 1.25 mmi. of crown glass with the mercury arc. Fig. 129 illustrates the relative fading of dyes on cotton when exposed to sunlight, the direct and the filtered mercury arc. The dyes are represented as rectangular strips, the degree of fading being represented by the part of the strip cut out. The sunlight fading is at one end and

FIGURE 129.
Relative Fading of Dyes on Cotton.



the filtered mercury arc fading at the other. The intervening fadings represent the effect of one-half hour and one hour exposure by the direct mercury arc and show the reversal of the relative fastness between the direct and basic dyes when exposed to the unfiltered mercury arc. Under this source silk and wool appear to have less reducing action on dyes than has cotton.

¹⁸⁸ Flynn, O. R., *Textile World*, 53, 25 (1923).

Iimori and Kitaoka¹⁰⁰ investigated the velocity of the bleaching of various dyes on cellulose acetate films before the mercury arc, but found it difficult to find one empirical equation which would express the behavior of every dye tested. Benzoic acid increased the rate of fading of methylene blue and disodium phosphate and calcium sulfate decreased it a little. For methyl violet, disodium phosphate, borax and quinine sulfate increased the rate slightly and calcium sulfate decreased it a little. Bravo¹⁰⁰ exposed a series of dyes on strips of filter paper at 50 cm. from a 2000 c.p. mercury lamp operated without a nickel oxide screen. The samples were ventilated to eliminate the possible influence of heat and ozone. One hundred and one dyes of the nitroso-, nitro- and azo- type were classified into four groups according to their resistance to bleaching. The very resistant dyes of Group I showed no change or only very slight changes after three hours. The resistant or medium-resistant dyes of Group II showed definite changes after two to three hours. Those of slight resistance (Group III) were altered in one to two hours. The non-resistant dyes of Group IV suffered intense changes in color or profound discoloration after one hour or less. Dyes of the nitro-, nitroso-, azo-, stilbene, pyrazolone, diphenylmethane and triphenylmethane, xanthene, acridine, quinoline, azine, oxazine and thiazine series were subsequently included. Bravo compared the percentage reflection at each of several wave-lengths photometrically with the corresponding values for a barium sulfate surface. In this way it was possible to study quantitatively the color changes which occur during fading.

Hill¹⁰¹ found the fading of worsteds dyed with Indigocarmine X, Ponceau RG and Neolan Green B to be chiefly dependent on the ultraviolet of shorter wave-lengths emitted by the mercury arc. A tungsten arc lamp of the Osram Co. of Berlin was claimed by Hochheim and Knebel¹⁰² to have a spectral distribution very similar to that of normal sunlight and therefore to be superior to the mercury arc.

It was early found by Gordon¹⁰³ that results with the violet carbon arc compare more closely to those of average sunlight than do those with the mercury arc. They agreed more closely with those of average sunlight than the results of Arizona and New Jersey sunlight agreed with each other. The white flame carbon arc gave rather better results in some cases but was only half as rapid as the violet arc. Mott and Bedford¹⁰⁴ stated that for equal line energy, the effect of the white flame arc on Solio paper was five to six times better than that of a 110-volt quartz mercury arc operating at four atmospheres at 60 arc volts.

Recently there has been great progress in the development of carbons which yield definite reproducible distributions of energy in various spectral regions; these have been discussed in Chapter 5. Various forms of apparatus employing the carbon arc have been put upon the market. In one form,¹⁰⁵ a number of "swatch boxes" in which samples of fabrics, paints, etc. may be exposed under definite conditions of humidity are arranged around a carbon arc. They are mounted on trunnions which are hollow and serve to supply conditioned air to all the boxes in series. When any swatch box is thrown down for inspection, the rotation of the trunnion causes the air stream to be by-passed around that box.¹⁰⁶

¹⁰⁰ Iimori, S., and Kitaoka, K., *J. Chem. Soc. Japan*, **48**, 479 (1927); *Chem. Abs.*, **22**, 1855 (1928).
¹⁰⁰ Bravo, G., *Bol. ufficiale staz. sper. ind. pelli mat. concianti*, **8**, 50, 184, 2928 (1930); **9**, 210 (1931).
Industria Chimica, **9**, 313, 461 (1934); *Brit. Chem. Abs.*, **B**, 711 (1934); *Chem. Abs.*, **25**, 2295, 3173 (1931); **28**, 4238, 6316 (1934).

¹⁰¹ Hill, L., *J. Soc. Dyers Colourists*, **43**, 296 (1927); *Brit. Chem. Abs.*, **B**, 839 (1927). Gordon, H. B., *Textile Colorist*, **43**, 29 (1921).

¹⁰² Hochheim, E., and Knebel, E., *Textilber.*, **6**, 912 (1925); *Brit. Chem. Abs.*, **B**, 437 (1926); *Chem. Abs.*, **20**, 669 (1926). See also Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 246 (1925); *Am. Dyestuff Rept.*, **14**, 882.

¹⁰³ Gordon, H. B., *Textile Colorist*, **43**, 29 (1921); *J. Soc. Chem. Ind.*, **40**, 149R (1921).

¹⁰⁴ Mott, W. R., and Bedford, C. W., *J. Ind. Eng. Chem.*, **8**, 1029 (1916). See also Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 42 (1925).

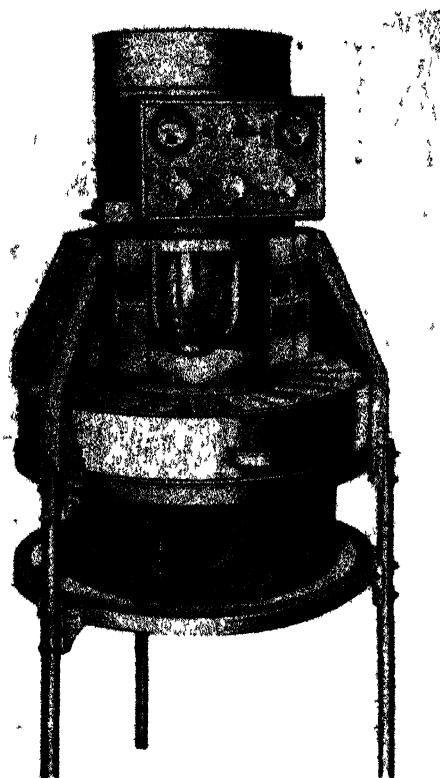
¹⁰⁵ King, F. A., *British P.* 309,726, April 2, 1928, to Kelvin, Bottomley and Baird Co.; *Brit. Chem. Abs.*, **B**, 461 (1929).

¹⁰⁶ For another form, see Hall, R. O., U. S. P. 1,969,606, to Ontario Research Foundation, and Bedford, E. F., *Silk J.*, **11**, No. 131, 38 (1935).

One of the most widely used types of commercial equipment is the Fade-Ometer (Fig. 130). In this, samples in metal specimen holders arranged in a circle are exposed to the light of a violet carbon arc enclosed in a 9200-PX glass globe. Ventilation is provided and the temperature is controlled by a thermostatically controlled blower. Textiles, papers and silks are generally tested between 98° and 104°F., but auto topping and similar materials are exposed at 140° to 150°F.

FIGURE 130.

Fade-Ometer, Type FDA.



Courtesy Atlas Electric Devices Co

A relative humidity of 42 to 60 per cent at the specimens is produced by wicks in a water reservoir placed below the specimen chamber. The air coming in contact with the specimens must filter through 1600 sq. in. of saturated wicking. The light from the source employed is so near that of sunlight that 95 per cent of a series of 40 dyes tested by it faded exactly as in sunlight or acceptably close to the sunlight fading. The light is somewhat more intense than sunlight so that for textiles one hour in the Fade-Ometer is equivalent to 13 hours of summer sunlight. For lithographic inks, 2.33 Fade-Ometer hours are approximately equivalent to six hours of sun exposure. In general for dyed textiles, 48 Fade-Ometer hours are equivalent to 10 days of summer or 180 days of winter sunlight. For printing inks, paper, etc., the 48 hour test is equivalent to 20 average days of summer or 360 days of winter sunlight.

Barker and Hirst¹⁹⁷ determined the fading of woollen and worsted patterns dyed with about 60 acid, direct, vat and mordant dyes in Indian, Ceylon and English sunlight and in the light of a Fade-Ometer. They used a Lovibond tintometer for direct visual comparisons and for measurements of the fluorescence in filtered ultraviolet light. By comparison of the fluorescence patterns it was possible to tell which samples had been faded in England, which in the tropics and which by the Fade-Ometer. The results in the latter case did not agree with those of exposure of the patterns to direct sunlight. Also less fading occurred in the tropics than in England. The discrepancies were attributed to the differences in the humidity.

The progressive loss of the predominant color in worsteds dyed with Indigo-carmin X, Wool Green S, Neolan Green B, Acid Violet 6B, Magenta and Ponteau RG and Chlorazol Blue B in the Fade-Ometer are given by the expression $t = \alpha l^n$ in which t is the time of exposure in hours, l is the percentage loss of predominant color, α is a constant which depends on the dye and n is 1.9 or 2.0. The actual and calculated color losses differ slightly during the early stages of fading.

Appel¹⁹⁸ recently concluded that the change in reflectance of some dyeings on exposure to light is not proportional to the intensity of the incident radiation, since when the intensity of the Fade-Ometer light was cut to one-tenth, the time required to produce a definite fading in different dyes was anywhere from two to ten times that required at the original intensity. Similarly, lowering the relative humidity from 75 to 31 per cent retarded the rate of fading of some dyes by a factor of two, but failed to affect the rate of fading of others.

Kinsman¹⁹⁹ employs the carbon arc and believes an exposure of 64 hours to be roughly equivalent to one month of summer sunlight. From comparisons of the results produced by the Fade-Ometer and sunlight, Griffith, Brode and Robertson²⁰⁰ conclude the former (Type LV) to be a satisfactory substitute for the latter. Peach, yellow and green pure dyed Tru-hu silk crêpe and yellow, blue and rose Peter Pan gingham were used in their tests. The blue gingham did not fade in either the sun or the Fade-Ometer; the rose gingham faded more in the sun, particularly in the blue-green portion of the spectrum. The yellow gingham faded only after exposure to 150 hours of sunlight or in the Fade-Ometer. The peach, yellow and green silk crêpes faded to the same extent with both sources.²⁰¹

Luckiesh and Taylor²⁰² noted that 23 silk ribbons exposed to sunlight and skylight at 3900 foot-candles for 11 hours, or to skylight alone at 450 foot-candles for 40 hours, showed as much fading as those exposed to 500 foot-candles from tungsten lamps for 100 hours. Approximately equal degrees of fading will result from exposure to the tungsten-filament radiation for 100 foot-candle hours, skylight for 34, or sunlight and skylight combined for 74.²⁰³

¹⁹⁷ Barker, S. G., and Hirst, H. R., *J. Soc. Dyers Colourists*, **43**, 254 (1927); Barker, S. G., Hirst, H. R., and Lambert, P. N., *Ibid.*, **263**, *Brit. Chem. Abs.*, **B**, 811 (1927); Barker, S. G., *J. Textile Inst.*, **18**, 313 (1927); *Chem. Abs.*, **22**, 2059 (1928).

¹⁹⁸ Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, **194**, 202, 1935; *Am. Dyestuff Rept.*, **24**, 306, 314 (1935); *Chem. Abs.*, **29**, 5276 (1935).

¹⁹⁹ Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Brit. Chem. Abs.*, **1930B**, 51.

²⁰⁰ Griffith, M. E., Brode, W. R., and Robertson, H., *Ohio Agr. Sta. Bi-monthly Bull.*, **169**, 143 (1934); *Chem. Abs.*, **28**, 7021 (1934).

²⁰¹ For a summary of early work on the suitability of various sources, see Hadfield, I. H., *J. Textile Inst.*, **18**, 527T (1927).

²⁰² Luckiesh, M., and Taylor, A. H., *Am. Dyestuff Rept.*, **14**, 613, 636 (1925); *Chem. Abs.*, **19**, 3597 (1925).

²⁰³ For observations on the effect of ultraviolet on certain dyes, see McEwen, J. L., *Am. Dyestuff Rept.*, **21**, 337 (1932).

Various Types of Dyestuffs. Heermann²⁰⁴ proposed to classify dye and textile fiber systems into four groups according to their susceptibility to light of various wave-lengths. These classes, termed "micro," "macro," "homo" and "mesotropic," are, respectively, most susceptible to light of short wave-lengths, long wave-lengths, all wave-lengths and to the ultraviolet rays of sunlight. Auramine, which is notoriously not fast to sunlight, resists short ultraviolet rays rather well.

In azo dyes,²⁰⁵ the naphtha dyes having a hydroxyl group in the 2-position are superior to those in which it is in the 1-position. The exceptions are 1-naphthol-4-sulfonic acid, which is comparatively fast, and 2-naphthol-3,6-disulfonic acid, which is fugitive. The presence of two sulfonic acid groups in the naphthol nucleus does not decrease the fastness of the dyestuff. *p*-Sulfanilic dyes are more affected than *o*-sulfanilic acid dyes but less than *m*-sulfanilic acid dyes. The degree of darkening is little influenced by the presence or position of the sulfonic acid group in the benzene nucleus, although there is slightly less darkening in the *o*- and *p*-sulfanilic acid dyes. The combined effect of fading and darkening, which gives the total effect of light on these dyes, indicates that the *o*-sulfanilic acid dyes are superior to those made from aniline and *p*- and *m*-sulfanilic acids.

Kinsman²⁰⁶ classifies lakes into five arbitrary groups according to the effects of light upon them. Group I, no perceptible alteration after one month in summer sunshine; II, slight loss; III, distinct loss in depth or alteration of shade; IV, distinct loss or alteration after 14 days; V, practically complete bleaching after one week. In practice, however, an accelerated test with a carbon arc was employed. Lakes belonging in the respective classes were as follows: I, Alizarin-red, aluminum calcium phosphate lake; II, Permanent-red 4B, calcium salt; III, Lithol-red R, barium salt; IV, Eosin YS, lead salt, barium sulfate base; V, lakes of fastness less than that of eosin. The carbon arc readings of these types are; unbleached after 240 hours, practically unbleached after 120 hours, bleached after 60 hours, bleached after 34 hours, bleached in less than 34 hours.

Wool patterns heavily dyed with Naphthol Yellow S, after exposure to sunlight until extensive browning had occurred, responded to a color test for 2-nitro-4-amino- α -naphthol-7-sulfonic acid, indicating the browning to be the result of photoreduction.²⁰⁷ The slow bleaching of annatto solutions by air is much more rapid in light.²⁰⁸

If dyed Celanese is treated with such organic bases as dimethylaniline or diethylaniline, which absorb wave-lengths shorter than about 3400Å, the light fastness of certain colors is improved. Colors strong in nitro- groups however, seemed to be deteriorated by this treatment.²⁰⁹ The best protection for airplane wings is to dye the dope with spirit black.²¹⁰

Colored Papers. Very similar methods are employed in testing the fading of dyes applied to paper. Appel and Bentzen²¹¹ recommend the Atlas Fade-

²⁰⁴ Heermann, P., *Chem. Ztg.*, **48**, 813, 834 (1924). For recent reviews see H. Niimiya, *Chem. Rev. (Japan)*, **3**, 401 (1937); Pierce, F. W., *Rayon Textile Monthly*, **19**, 249, 263 (1938), Volz, K., *Spinnere u. Weber*, **56**, No. 34, 43, 53 (1938).

²⁰⁵ Griffith, M. E., *Ohio Agr. Expt. Sta., Bull. No. 548*, 80 (1935); Griffith, M. E. and Brode, W. R., *Ibid.*, **Bull.** **565**, 3 (1936); *Am. Dyestuff Rept.*, **26**, 90 (1937); *Chem. Abs.*, **30**, 1565 (1936); **31**, 1211 (1937).

²⁰⁶ Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Chem. Abs.*, **24**, 737 (1930).

²⁰⁷ Hodgson, H. H., and Smith, E. W., *J. Soc. Chem. Ind.*, **56**, 108T (1937); *Chem. Abs.*, **31**, 4500 (1937).

²⁰⁸ Barnicoat, C. R., *J. Dairy Research*, **8**, 61 (1937); *Chem. Abs.*, **31**, 3581 (1937).

²⁰⁹ Ellis, G. H., *Chem. Age*, **13**, 470 (1925); *J. Soc. Chem. Ind.*, **44**, 1093 (1925).

²¹⁰ First Report Fabrics Coördinating Research Committee, Dept. Sci. Ind. Research, **10** (1925); *Chemical Age (London)*, **13**, 331, 397 (1925).

²¹¹ Appel, W. D., and Bentzen, T., *Paper Trade J.*, **88**, No. 9, 42 (1929); *Chem. Abs.*, **23**, 3095 (1929); Dalen, G., and Wilke, P., used the mercury arc, *Papier-Fabr.*, **26**, 199; *Chem. Abs.*, **22**, 2272 (1928).

Ometer, particularly the type equipped with a fan to prevent excessive heating of the sample. Grundy,²¹² who also approved the method, noted that the exposed dyeings should be allowed to cool a short time before comparing the colors, since a slight change in shade may be due to the heat of the arc, rather than to fading. It did not seem possible to make standard numerical specifications for the light-fastness of colors on all qualities of paper. No basic colors were found which had sufficient fastness to receive consideration for the production of fast-to-light shades. With the ordinary type of soluble synthetic dyestuffs generally applied on paper, it seemed impossible to obtain fast shades on furnishes containing even small quantities of brown wood. The most suitable furnishes for fast-to-light shades are bleached sulfite, bleached soda, esparto, bleached rag, and under certain conditions unbleached sulfite, either individually or in mixture.

Loading materials affect the light fastness of dyes in paper,²¹³ partly because of the alkalinity of the filler. The pH of filled or unfilled papers is generally reduced by exposure to sunlight. Papers of lower pH values are the more easily faded. Dyes which are fast to light are generally acid resistant.

Riesenfeld and Hamburger²¹⁴ employed the time of exposure to a standard ultraviolet source required to produce a definite change in fluorescence as a measure of the relative light fastness of dyed papers.

Harrison²¹⁵ did not approve the use of the Grant method of following the reduction of fluorescence on irradiation, but could find no suitable inexpensive daylight lamp for comparing the samples. He proposed the use of bleached sulfite pulp, colored with graduated amounts of fast dyes, including the Chlorantin colors, or using one amount with additions of hexadecylpyridinium bromide to decrease the fastness. The sheets were then exposed to direct sunlight for 6, 12, 24, 48 and 96 hours and compared with controls or with irradiated controls without the addition of the deteriorating agent. He measured the light intensity to which the sample was exposed by an actinometric paper and a wedge-shaped slide transmitting graded amounts of light. This, when laid over a standard colored sheet, simulates the effect of graded bleaching. With this method, the best results were obtained with a pure rag paper, sized with 2 per cent rosin and 4 per cent alum, and dyed with Acid Rhodamin 3R.

Inks. Proposals have been made to employ ultraviolet radiations for testing inks by measuring the color of streaks on paper after exposure for two weeks to sunlight or for a shorter period to ultraviolet light.²¹⁶ The Bureau of Standards²¹⁷ recommended an exposure of 48 hours to ultraviolet light. A comparison streak of a standard ink was simultaneously exposed. Turner²¹⁸ classified about fifty pigments into four groups according to their light fastness in printing ink.

Tests by Mitchell²¹⁹ did not substantiate the claim that ultraviolet fluorescence tests can be used for the differentiation of different types of inks or for the determination of their ages.

²¹² Grundy, J. G., *World's Paper Trade Rev.*, **101**, 1240, 1242, 1280, 1399, 1442 (1934); *Paper Maker and British Paper Trade J.*, **88**, No. 1, 138 (1934), *Chem. Abs.*, **28**, 7010 (1934).

²¹³ Pestalozzi, S., *Zellstoff u. Papier*, **15**, 496 (1935), *Chem. Abs.*, **30**, 1558 (1936).

²¹⁴ Riesenfeld, E. H., and Hamburger, T., *Papier-fabr.*, **29**, 164 (1931); *Brit. Chem. Abs.*, **B**, 625 (1931).

²¹⁵ Harrison, H. A., *Papier-Fabr.*, **34**, *Tech. Teil*, 321, 329 (1936); *Chem. Abs.*, **31**, 856 (1937); *Paper-Maker*, **TS 54** (1936); *Chem. Abs.*, **31**, 2428 (1937); *Svensk Papperstidn.*, **39**, 352 (1936).

²¹⁶ Rupert, F. F., *Ind. Eng. Chem.*, **15**, 489 (1923), *J. Soc. Chem. Ind.*, **42**, 612A (1923).

²¹⁷ *Bureau of Standards Circular 95* (1920).

²¹⁸ Turner, J. S., *Am. Ink Maker*, **14**, No. 1, 19 (1936); *Chem. Abs.*, **30**, 5817 (1936); Deeney, J. J., *Am. Ink Maker*, **11**, No. 2, 9, 23; No. 3, 13 (1933) (*Chem. Abs.*, **27**, 5557 (1933)).

²¹⁹ Mitchell, C. A., *Analyst*, **55**, 746 (1930).

Ink on freshly printed sheets dries faster when exposed at a distance of six inches from a mercury arc than in diffused lights, especially at higher temperatures.²²⁰

In making hectograph copying pads, a gelatinous mass (gelatin, water and glycerol) is treated with a minute proportion of a light-sensitive tanning agent such as ammonium dichromate and subjected to the action of ultraviolet light to effect tanning.²²¹

Fluorescence Tests of Dyes. Hirst and King²²² found that certain Indigo-sol dyes on wool showed in ultraviolet light a strong violet fluorescence on the original dyeing, but not on portions which had been exposed to light for some weeks. They suggested that the fluorescence might indicate incomplete oxidation and incomplete development since its intensity varied when different oxidizers were used. The method also could be used for indicating the degree of exhaustion of the dye-bath and was thought of value in the control of this type of dyeing. Kummerer²²³ tabulated the fluorescence colors in ultraviolet light of variously dyed fabrics. The determination of fibers by their fluorescence colors is, according to Sommer,²²⁴ subject to distinct limitations. For example, the dye present may entirely obscure the fluorescence color of the fabric or even lead to false conclusions. No certain distinction could be made between dyed flax and hemp. Bleached linen and cotton could not be distinguished nor could mohair and wool. Egyptian cotton is readily determined, as is dyed wool intended as a substitute for camel hair. Oil spots on fabrics are especially distinct. Alkali or acid damage to wool is not determinable by this method. After sulfite cellulose pulp has been exposed to a bright light it cannot be distinguished in this manner from soda pulp. The method cannot be used to identify coloring matters, according to Radley.²²⁵

TEXTILE PRINTING²²⁶

Haendel²²⁷ described a process in which woven and knitted or plaited fabrics, leather and other materials are dyed or figured by treating them with light-sensitive compounds and subsequently exposing them to the action of light. Substances may be used which form dyes when exposed to light, such as mixtures of a sulfonated diazo- compound, *e.g.*, sodium phenyldiazosulfonate and an azo- component such as aniline hydrochloride. Light-sensitive substances which lose their capacity to form dyes when exposed to light may be used.

Designs may be applied to yarns, bands or fabrics of non-animal origin in a continuous operation involving application of a metal compound convertible photochemically into a compound in which the valence of the metal is different, exposure to ultraviolet light passing through a pattern, washing, conversion of either

²²⁰ Brown, R. A., *Am. Ink Maker*, 9, No. 3, 21 (1931); *Chem. Abs.*, 25, 3500 (1931). The carbon arc is used by Arend, A. G., *Process Engraver's Monthly*, 44, 173 (1937).

²²¹ Whitmore, W. B., U. S. P. 2,024,408, Dec. 17, 1935, to Ditto, Inc.; *Chem. Abs.*, 30, 1156 (1936).

²²² Hirst, H. R., and King, A. T., *J. Soc. Dyers Colourists*, 43, 266 (1927); *Chem. Abs.*, 22, 2276 (1928); *J. Textile Inst.*, Special No., 18, 369T (1927); *Chem. Abs.*, 22, 2061 (1928).

²²³ Kummerer, L., *Melliand Textilber.*, 9, 415 (1928). Sisley, P., [*Chimie et industrie, Special number 508* (March 1932)] gives data on 1200 dyes.

²²⁴ Sommer, H., *Melliand Textilber.*, 9, 753 (1928); *Chem. Abs.*, 22, 4825 (1928); compare de Buda, G., *Cuir tech.*, 21, 98 (1932); *Chem. Abs.*, 26, 3115 (1932).

²²⁵ Radley, J. A., *J. Soc. Dyers Colourists*, 53, 376 (1937); *Chem. Abs.*, 32, 364 (1938).

²²⁶ In the decoration of fabrics by the reducing action of light on silver salts, Michels, M., [*German P.* 441,690, May 4, 1926; *Bull. soc. ind. Mulhouse*, 94, 124, 135 (1928); *Chem. Abs.*, 22, 2468 (1928)] uses as a mordant for all basic dyes, a material formed from complex copper compounds.

²²⁷ Haendel, W., *British P.* 309,166, April 7, 1928; *Chem. Abs.*, 24, 509 (1930).

the altered or unaltered portion of the metal compound into a substance which cannot be washed out, washing and drying.²²⁸

In an example, linen is passed through potassium dichromate solution, then over a rotary stencil containing one or more carbon arc lamps or mercury discharge tubes, treated with sodium alizarine sulfonate solution after passing through water, washing and drying.²²⁹

Freytag²³⁰ showed that ultraviolet irradiation of solutions containing aniline hydrochloride and suitable oxidizing agents and catalysts as used in aniline black dyeing markedly accelerates the formation of the aniline black pigment. Satisfactory reproduction of images may be obtained by impregnating paper or cotton fabric with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of aqueous 4-per cent potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous sodium chlorate per 30 cc., covering with a photographic negative and exposing for fifteen minutes to ultraviolet light, and washing out unchanged aniline with water.

Similarly, solutions of either of the phenylenediamines produce a yellow or brown color formed by oxidation of the base. The naphthylamines behave in an analogous manner.²³¹ The process is assisted by the presence of about 1 per cent of an alkaline nitrate in the naphthylamine bath. With β -naphthylamine, the process is very rapid and will take place even in sunlight.

Freytag and Müller²³² also employed 2-benzyl pyridine, which becomes deep brown on exposure to light. Radiation of 2000 to 4000 Å converts it into a green dye. The compound is applied in 96-per cent alcohol and the solvent evaporated before making the exposure to light through a negative. The excess of unaltered compound is removed with dilute hydrochloric acid. The fastness of the photopyridine colors can be improved by coupling with diazotized bases.²³³ After exposure for thirty to forty-five minutes at 30 to 50 cm. from a quartz lamp, the sample is passed through a boiling acid bath containing two to three per cent of a primary aromatic amine. The color thus obtained lacks fastness, but this may be improved by treating it without washing with a solution of a diazonium salt of an aromatic base. There is considerable change in the color.

Benzidine and tolidine on irradiation in the presence of sodium nitrate are oxidized on the fiber to fast dyes.²³⁴ The samples of cotton and artificial silk so treated are coffee-brown with benzidine and yellowish-brown with *o*-tolidine. A number of amino-naphtholsulfonic acids have also been used.²³⁵ The most suitable substances are the pyridines and the aniline salts of 8-nitro-1-naphthalenesulfonic acid. The best results are obtained when the exposures are made in a damp atmosphere.

Stabilized isodiazotate solutions²³⁶ of aniline, *p*-brom- and *p*-iodo- aniline, etc.

²²⁸ British P. 380,208, April 23, 1931, to N. V. Phillips Gloeilampenfabrieken; French P. 768,261, Aug. 3, 1934; *Chem. Abs.*, **27**, 3087 (1933); **29**, 621 (1935).

²²⁹ For a general discussion of printing by photochemical processes, see Weickart, F., *Monatsh. Seide, Kunstseide*, **38**, 474 (1933).

²³⁰ Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

²³¹ Freytag, H., *Phot. Korrr.*, **69**, 184 (1933); *Chem. Abs.*, **28**, 7538 (1934).

²³² Freytag, H., and Müller, A., *Monatsschr. Textilind.*, **48**, 239, 273 (1933); *Chem. Abs.*, **28**, 5245 (1934).

²³³ Freytag, H., *Monatsschr. Textilind.*, **48**, 107, 130 (1933); *Chimie et industrie*, **31**, 621; *Chem. Abs.*, **28**, 3590 (1934).

²³⁴ Freytag, H., and Preiss, S., *Monatsschr. Textilind.*, **49**, 209, 231 (1934); *Chem. Abs.*, **29**, 2362 (1935).

²³⁵ *Monatsschr. Textilind.*, **49**, 262 (1934); *Chem. Abs.*, **29**, 2362 (1935); *Phot. Korrr.*, **71**, 52 (1935).

²³⁶ Oddo, G., Indovina, R., Albanese, G., and Amatore, G., *Gazz. chim. ital.*, **65**, 939 (1935); *Chem. Abs.*, **30**, 3792 (1936).

again acquire the power of coupling after thirty minutes of exposure to sunlight, ultraviolet light or an ordinary incandescent lamp. This is of importance in the dyeing and printing of textiles, since it is unnecessary to treat the salts with hydrochloric acid to form diazonium salts and to couple these with alkaline β -naphthol or other phenols, or with a base, but only to expose the solutions with the other azo- component to heat, sunlight or ultraviolet light. It may also be of importance in negative diazo-printing. It was found possible with the halogenated bases easily to reproduce not only the image of any object impenetrable to sunlight, but also the colored image of the negative obtained by the ordinary photographic process.²³⁷ The effect is not observed with *o*-toluidine, 1,3,4-xylydine, pseudocumidine and mesidine. Acidification of the alkaline coupling solution of diazotized aniline and acetamide gave a colorless precipitate which when dried rapidly in darkness was found to have the composition and molecular weight of acetyl-phenyltriazene. The crystals became reddish yellow in diffused light and after two weeks were a beautiful dark red. During this process the melting point dropped from 101 to 96°C.²³⁸

Cloth treated with certain vat dyes and dried may also be printed under a negative until the desired oxidation is complete, after which the unoxidized portion of the dye is removed by a boiling soap solution.²³⁹ The dyes sensitive to ultraviolet include Indigosol Orange HR, Scarlet HR and Pink IIR. Indigosol 4B and HB are less sensitive to sunlight.

PHOTOGRAPHIC PAPERS

In obtaining photographic images, Gay²⁴⁰ mixed light-sensitive diazo- compounds with O-acyl derivatives of the phenols or naphthols, used as coupling components in development. The phenols or naphthols are liberated by development with ammonia gas or a dilute alkaline bath and a colored positive image is obtained.

For diazotypes, Kalle & Co.²⁴¹ use a diazo- compound capable of self-coupling in alkaline media applied in neutral or acid solution to the support. After exposure under a positive, the print is developed with gaseous ammonia. Suitable diazo- compounds are those from H-acid, 3-amino-6-N-piperidinobenzoyl-H-acid and 2,7-aminonaphthol.

Spencer²⁴² states that diazo- compounds for photographic papers should be sufficiently sensitive to light, and stable toward heat, mechanical shock, and to the paper base upon which they may be coated in sufficient concentration by the use of an inert solvent. They should couple readily with amines and phenolic compounds to give dark-colored substances insoluble in water and stable to light. The decomposition products should not interfere with the color or stability of the image. The following types of paper are possible: (a) the diazo- compound is decomposed by light and is developed by application of an alkaline coupler which reacts only with the unchanged diazo- compounds; (b) the diazo- compound and coupler are coated together, but reaction is prevented by the presence of an organic

²³⁷ Oddo, G., and Indovina, R., *Gazz. chim. ital.*, **65**, 1037, 1099 (1935); *Chem. Abs.*, **30**, 4830 (1936).
²³⁸ Oddo, G., and Algerino, A., *Ber.*, **69B**, 279 (1936); *Chem. Abs.*, **30**, 3418 (1936). For a discussion of visible light effects in certain phenyldibenzoxanthrenium dyes, see Dilthey, W., and Quint, F., *Ber.*, **69B**, 1575 (1936).

²³⁹ Cowper, W., *Dyer, Calico Printer*, **58**, 117 (1927); *Chem. Abs.*, **22**, 1045 (1928).

²⁴⁰ Gay, E., *British P.* 282,894 and 283,274 (1926); *Brit. Chem. Abs.*, **B**, 173 (1928).

²⁴¹ *British P.* 297,363, Aug. 19, 1928, to Kalle and Co.; *Brit. Chem. Abs.*, **B**, 350 (1930)

²⁴² Spencer, D. A., *Phot. J.*, **68**, 490 (1928); *Brit. Chem. Abs.*, **B**, 73 (1929).

acid, such papers being developed by weak alkali solutions or ammonia vapor; (c) the diazo- compound is coated with a coupler in an unreactive state, *e.g.*, as an additive compound, development being effected by breaking up the additive compound by heat, ammonia, etc.; (d) the diazo- compound is decomposed by light into a substance which will react with the original diazo- compound either on keeping or in the presence of alkali.

A combination of boric acid and an organic acid (citric, tartaric) is more efficient than the organic acid alone in preventing the premature formation of coloring matters in diazo- papers in which the coupling agent and the diazo- compound are applied together.²⁴³ A suitable coating mixture is: stannic chloride double salt of 4-diazo-1-dimethylaniline, 22, boric acid, 20, tartaric acid, 50, phloroglucinol 2 and water 1000 parts. Preservation by depriving the surface of moisture during the preparation is also described.²⁴⁴

Neuroth²⁴⁵ prepared light-sensitive layers by bringing aryl azides onto a support together with phenols, aromatic amines or aminophenols. Development of the exposed layer is effected by washing out the unreacted azide or by rendering it inactive by reduction.²⁴⁶

Schmidt and Spietschka²⁴⁷ described the manufacture of light-sensitive paper from diazo- compounds of aminonaphtholcarboxylic acids, such as 1-diazo-2-hydroxy-3-naphthoic acid in sodium hydroxide. If exposed beneath a negative and washed with water, a blue-black print on a pure white ground is obtained. Schmidt and Zahn²⁴⁸ add a compound other than a dye showing strong ultraviolet absorption, as sodium 6-phenyl-2-aminopseudo aziminobenzene-3,4'-disulfonate, to inks, or crayons for making drawings from which blue prints are to be prepared, in order to secure clearer reproduction.

Miscellaneous Processes. In a photographic method for the reproduction of natural wood grains, the softer parts of the wood are removed by chemical and mechanical means. The pattern is then fixed on a photographic plate from which the printing surface is produced. The treated wood may be illuminated by ultraviolet light for reproduction or may be directly printed by x-rays.²⁴⁹

Beebe²⁵⁰ described a compound adapted for reproducing designs on metal, glass, etc. which comprises a varnish containing a light-sensitive oil (tung) and an accelerator (iodine) which serves to accelerate the action of light on the varnish for photographic purposes.

On the assumption that cellulose products as ethers or esters, papers, artificial soaps, etc., on exposure to ultraviolet light become permeable to gases, vapors or liquids, Kleiner,²⁵¹ patented a method for the production and reproduction of pictures or designs by visible or invisible rays.

²⁴³ British P. 294,247, July 16, 1928, to Kalle & Co.; *Brit. Chem. Abs.*, **B**, 1033 (1929).

²⁴⁴ N. V. Phillips' Gloeilampenfabrieken. French P. 794,590, Feb. 20, 1936; *Chem. Abs.*, **30**, 5137 (1936).

²⁴⁵ Neuroth, H., German P. 510,165, Oct. 22, 1929, to Kalle & Co.; *Chem. Abs.*, **25**, 886 (1931).

²⁴⁶ See also Werner, G., U. S. P. 2,063,832; *Chem. Abs.*, **31**, 620 (1937); Alink, R., U. S. P. 2,083,285; *Chem. Abs.*, **31**, 5285 (1937).

²⁴⁷ Schmidt, M. P., and Spietschka, W., German P. 470,088, Dec. 11, 1927, to Kalle & Co.; *Chem. Abs.*, **25**, 466 (1931).

²⁴⁸ Schmidt, M. P., and Zahn, R., German P. 517,159, July 24, 1926, to Kalle & Co.; *Chem. Abs.*, **25**, 2066 (1931).

²⁴⁹ British P. 308,373-4-5-6, March 22, 1928, to Masa G.m.b.H. zur Herstellung künstlicher Oberfläche; *Chem. Abs.*, **24**, 32 (1930). See also for another process, R. R. Tanner, U. S. P. 2,127,944, Aug. 23, 1938; *Chem. Abs.*, **32**, 7840 (1932).

²⁵⁰ Beebe, M. C., U. S. P. 1,574,356-7-8-9, Feb. 23, 1926; *Chem. Abs.*, **20**, 1362 (1926).

²⁵¹ Kleiner, S., British P. 413,095, April 26, 1933; *Chem. Abs.*, **29**, 417 (1935).

Polden²⁵² employs light or ultraviolet radiations or electric currents at super-atmospheric pressures to accelerate the bleaching of tortoise shell and similar natural materials by bleaching agents that yield nascent oxygen, such as hydrogen peroxide.

²⁵² Polden, D. C., British P. 429,524, May 31, 1935; *Chem. Abs.*, **29**, 7531 (1935).

Chapter 33

Miscellaneous Applications of Ultraviolet Light

An application of the polymerization of oils by ultraviolet light is to be found in the production of patent leather. It has been claimed that the exposure of the varnished surfaces to the action of a mercury-vapor lamp gives the same result in one and one-half hours as is obtained by several days of exposure to sunlight. The method is not, however, widely used.

One process is carried out in an atmosphere containing ammonia derivatives, nitrogen, hydrogen or other neutral gases,¹ or in an exhausted chamber. The leather is carried on frames in the chamber, quartz lamps being arranged between the frames.² Lombard³ claims that better results are obtained if the extreme ultraviolet rays are filtered out.

An apparatus for the treatment described by Priest,⁴ comprises a frame arranged on bearings which serves as a support for the hides which are to have their varnished surfaces exposed to the direct action of the ultraviolet rays. The action of the rays from a series of quartz lamps vertically arranged in the center of the revolving frame may be supplemented by the action of ozone.

Stoeckly⁵ used ultraviolet rays produced by a high-frequency spark discharging thirty to sixty times per second, each spark consuming about 0.7 kilowatt. Prior to the use of artificial ultraviolet sources, the stock coated with the linseed oil varnish mixture was exposed to the direct rays of the sun for eight to ten hours. Such drying was greatly retarded by a humid atmosphere. Dinsley and Pulman⁶ suggested subjecting leather to the ultraviolet rays prior to enameling it. Other patents dealing with structural features of the apparatus employed are due to Hughes,⁷ and to Elliott⁸

The kind of plasticizer is of primary importance in determining the rate of deterioration of nitrocellulose films in artificial leather if embrittlement and insolubilization of the surface on exposure to light are to be avoided.⁹ Anderson and Lamb¹⁰ studied the properties of films containing various plasticizers, added to the extent of 0.25 to 2.0 per cent to films from a 3-per cent solution of Cotton 8A (nitrocellulose) in equal parts of butyl acetate and butyl alcohol. The films were formed by flowing on glass and exposing to the mercury arc. Of the eight plasticizers studied, "Sipaline AOM" (dimethylcyclohexyl adipate) gave the best results as regards flexibility and durability on exposure to ultraviolet light. Triacetin is also recommended for leather which requires much stretching.

¹ Heyl, C., British P. 113,622, Feb. 21, 1918; Swiss P. 76,436, Dec. 17, 1917, British P. 113,620, Feb. 20, 1918.

² See also Swiss P. 77,117 and 77,378; Dutch P. 1,970; Danish P. 22,258 and 22,269; Hintz, E., *J. Soc. Chem. Ind.*, **37**, 709A (1918), *Chem. Abs.*, **12**, 1935 (1918); U. S. P. 1,269,931, June 18, 1918.

³ Lombard, V. G., *J. Am. Leather Chem. Assn.*, **10**, 86 (1915); cf. Lattey, W. T., *J. Oil and Colour Chem. Assoc.*, **9**, 45 (1926); *Brit. Chem. Abs.*, **B**, 377 (1926).

⁴ Priest, G. W., U. S. P. 1,262,977, April 16, 1918; *J. Soc. Chem. Ind.*, **37**, 343A (1918).

⁵ Stoeckly, J. J., British P. 148,454 and 149,334, 1920; *Chem. Abs.*, **15**, 329, 450 (1921).

⁶ Dinsley, A., and Pulman, A. O., British P. 190,781, Sept. 23, 1921; *J. Soc. Chem. Ind.*, **42**, 193A (1923).

⁷ Hughes, W. A., U. S. P. 1,747,301, Feb. 18, 1930, to Cooper-Hewitt Electric Co.

⁸ Elliott, E. I., U. S. P. 1,702,043, Feb. 12, 1929, see also Brophy, J. J., U. S. P. 2,020,296, British P. 452,618, Oct. 26, 1935; *Brit. Chem. Abs.*, **B**, 1109 (1936).

⁹ Genin, G., *Halle aux cuirs*, 67, (1932); *Chem. Abs.*, **26**, 3136 (1932).

¹⁰ Anderson, H., and Lamb, M. C., *Cuir tech.*, **23**, 130 (1934); *Chem. Abs.*, **28**, 5999 (1934).

Ultraviolet rays shorter than 3000A rapidly darken leather. This property can be used to produce designs on leather by the aid of stencils or Uviol glass photographic plates.¹¹ The darkening is caused by an iron-tannin compound. Light activates or frees both tannin and iron. Inorganic or organic compounds can be used to increase the depth and permanency of the designs or to alter their shade.

All vegetable-tanned leathers darken on exposure to light, frequently with a loss of strength, but ¹² this is most marked in leathers tanned with catechol tannin. Attempts to find an effective inhibitor have been unsuccessful. The presence of water is necessary for darkening in ultraviolet light.

Fluorescence analysis methods have found application in leather chemistry.¹³ Cuccudoro ¹⁴ believed it possible by such methods to assist in distinguishing between the various components of raw hide, that is, collagen, keratin, bloody tissues, and tanning materials. They also were found useful in determining the depth of penetration of vegetable tannins and the saturation of the hides with such materials and also in the examination of finished leather for indications as to the manufacturing processes which had been employed.¹⁵

The absorption spectra of solutions of various tanning materials have been measured by de la Bruère.¹⁶

The use of the ultraviolet microscope, which combines increased resolving power with the advantages of fluorescence, is finding application in the study of animal skin.¹⁷

PETROLEUM PRODUCTS

Absorption Studies. Crude petroleum oils are characterized by absorption bands with maxima at about 3000, 2800, 2650, 2420 and 2400A due probably to cyclic hydrocarbons¹⁸ Transformer oils of various origins cannot be distinguished by ultraviolet absorption spectra. Aging of the oils merely decreases the sharpness of the bands.¹⁹

It has been stated that benzene, xylene and toluene can be readily determined in gasoline by ultraviolet absorption studies. Relatively little has, however, been written regarding the absorption of light by various petroleum products.²⁰ Schou and Bendix-Nielsen ²¹ find the absorption of a band at 2730A in samples of liquid paraffin parallels the results of the sulfuric acid test for organic impurities.

Mineral oils dissolved in various solvents change color on exposure to light according to the nature of the solvent.²² Carbon tetrachloride, chloroform and amyl alcohol are the most active, but no changes take place in acetone and ether. In the absence of air, the discoloration is probably due to soluble polymerization products.

¹¹ Freytag, H., *Collegium*, 161, (1932); *Chem. Abs.*, 26, 3955 (1932), French P. 707,490.

¹² Woodroffe, D., *J. Internat. Soc. Leather Trades Chem.*, 18, 424 (1934); *Chem. Abs.*, 28, 6340 (1934).

¹³ Deforge, A., *Halle aux cuirs*, 36, 83 (1928); Grasse, G., *Cuir tech.*, 20, 141 (1931).

¹⁴ Cuccudoro, M., *Boll. ufficiale staz. sper. ind. pell. mat. concianti*, 10, 237 (1932); *Chem. Abs.*, 27, 624 (1933).

¹⁵ Further reviews of these methods have been given by Desmurs, G., *Cuir tech.*, 21, 40, 57, 77 (1932); Karsten, A., *Leder tech. Rundschau*, 26, 93 (1934), *Cuir tech.*, 23, 330 (1934); 24, 36 (1935); 24, 198 (1935). Karsten described a fluorescence microscope for use in the leather industry.

¹⁶ de la Bruère, A., *J. Soc. Leather Trades Chem.*, 9, 427 (1925); *Chem. Abs.*, 19, 3384 (1925); Deforge, A., *Halle aux Cuirs*, 131 (1929).

¹⁷ Theis, E. R., and Serfass, E. J., *J. Am. Leather Chem. Assoc.*, 33, 67 (1938).

¹⁸ Vlès, F., and Gex, M., *Compt. rend.*, 180, 140 (1925).

¹⁹ Vellinger, E., and Klinkenberg, A., *Ann. combustibles liquides*, 10, 79 (1935); *Chem. Abs.*, 29, 1815 (1935).

²⁰ Luszcak, A., *Abhandl. Gesamtgebiete Hyg. No. 22*, 59 (1926); *Chem. Abs.*, 31, 4801 (1937). Certain photochemical reactions of Russian petroleum have been discussed by Pyhäälä, E., *Mat. grasscs.*, 23, 9124, 9182 (1931).

²¹ Schou, S. A., and Bendix-Nielsen, I. B., *Dansk Tidskr. Farm.*, 4, 1 (1930); *Brit. Chem. Abs.*, B, 263 (1930); *Arch. Pharm.*, 272, 761 (1934); *Chem. Abs.*, 29, 915 (1935).

²² Vellinger, E., and Marchand, P., *Ann. combustibles liquides*, 5, 977 (1930); *Chem. Abs.*, 25, 4391 (1931); Vellinger, E., *Ann. combustibles liquides*, 12, 195, 250 (1937); *Chem. Abs.*, 31, 7629 (1937).

With air, the change in color is not as distinctive, but insoluble oxidation products are formed. Shile and Avakova²⁸ find paraffin containing more than 0.1 per cent of oil to be unstable toward ultraviolet rays. Such paraffin, treated with fullers' earth and exposed to ultraviolet rays, is light-stable.

Heavy liquid pharmaceutical petrolatums of different geographical origins differ considerably in resistance to spoiling by exposure to sunlight in flint glass bottles.²⁴ The light-stability can be measured by comparatively short exposures of the oil in flint bottles to ultraviolet light.

It was once suggested that ultraviolet light be employed in the cracking of petroleum oils. They were to be heated with a catalyst and sprayed through an irradiated zone.²⁵ A patent to Physical Chemistry Research Co.²⁶ described the preparation of liquid hydrocarbons suitable for use as fuels by distilling solid fuels and subjecting the resulting gases, together with carbon monoxide and hydrogen, to the action of both ultraviolet rays and a high-potential electrostatic field.

Egloff²⁷ heats normally incombustible hydrocarbon gases from oil-cracking under superatmospheric pressure to about 650 to 1000°C., then lowers the pressure on the gases and subjects them to the action of ultraviolet light.²⁸

Miller²⁹ renders solar light petroleum distillates, refined by treatment with silica gel, sweet to the "doctor test" by exposure to the radiations from a mercury-vapor lamp. Morrell³⁰ treats hydrocarbon distillates containing mercaptans by converting them to mercaptides by treatment with "Sunlite" solutions and then precipitates the mercaptides by exposing the products to ultraviolet light.

The bloom or fluorescence of petroleum oil may be destroyed by ultraviolet rays.³¹ Some oils are thereby reddened in color or otherwise slightly darkened. Other oils are bleached by such treatment. Petroleum oils intended for use as lubricants and which may have gumming properties due to unsaturated components are improved in quality by exposure to ultraviolet rays in an inert gas. Apparently polymerization occurs, resulting in the formation of saturated bodies. Gray³² deblooms lubricating oil, paraffin wax and the like and brings about partial conversion to acids and esters by blowing air through the hydrocarbon material at 50 to 120°C., while exposing it to ultraviolet rays. Catalysts may be present and the operation may take place at pressures up to five atmospheres. Gray states that he has been able to convert 75 per cent of the hydrocarbon material into fatty acids by this process.

Color Changes. Gasolines refined from certain California crude oils not treated by clay or acid tend to take on a color which may be pink, yellow or light chocolate when the product is dispensed in a visible pump in the presence of sunlight. McConnell³³ proposed to treat such oils by exposing them to daylight for

²⁸ Shile, V. N., and Avakova, E. S., *Nestyanoe Khozyaystvo*, 25, No. 9, 59 (1933), *Chem. Abs.*, 28, 4886 (1934).

²⁴ Green, L. W., and Schoetzow, R. E., *J. Am. Pharm. Assoc.*, 21, 1286 (1932); *Chem. Abs.*, 27, 1987 (1933).

²⁵ French P. 469,948, 1914, to Continental Caoutchouc and Gutta-Percha Co.

²⁶ British P. 357,206, June 4, 1929, to Physical Chemistry Research Co.; *Chem. Abs.*, 26, 4701 (1932).

²⁷ Egloff, G., U. S. P. 1,904,362, April 18, 1933, *Brit. Chem. Abs.*, B, 134 (1934).

²⁸ For a patent relating to the utilization of ultraviolet rays for supporting combustion in heat engines, see Gill, H. A., British P. 269, 808, Nov. 9, 1926.

²⁹ Miller, E. B., U. S. P. 1,647,459, Nov. 1, 1928; *Chem. Abs.*, 22, 315 (1928).

³⁰ Morrell, J. C., U. S. P. 1,904,382, April 18, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 27, 3601 (1933).

³¹ Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914.

³² Gray, T. T., U. S. P. 1,158,205, Oct. 26, 1915.

³³ McConnell, J. R., U. S. P., 1,590,841; June 29, 1926; *Chem. Abs.*, 20, 3077 (1926).

fifteen to thirty or more daylight hours to fix the color or complete the color reaction to its maximum and then remove the discoloring compound, preferably by distillation. In this process, the sensitive portion, which is probably an organic sulfur compound, is rendered non-volatile and remains in the residue on distillation. The distillate then retains its freedom from color on exposure to sunlight. The process is known as complete fixation. It is said that the process may also be applied to the first pressure distillate of cracked gasoline and so obviate the necessity of treating a large percentage of the cracked gasoline with either acid or clay.

Even paraffin has been improved in its fastness to light by treating it with decolorizing agents and radiations of short wave-lengths together or in turn. Oxygen may be supplied during the irradiation.³⁴

Kovalev and Illarionov³⁵ exposed Grozny petroleum distillates to sunlight for three months with free access of air. Kerosene, light and heavy solar oil, spindle oil, engine oil and cylinder oil were used. The specific gravity and refractive indices of the samples changed very little. The dielectric constant increased at first, but after two months decreased. The drop in the third month is explained by supposing that rearrangement takes place in an oxygen compound, the added active oxygen being given to other unsaturated molecules forming ketoxy and oxy-compounds. No aldehydes were found. Panchenkov and Puzitskii,³⁶ however, state that certain wave-lengths increase the viscosity of lubricating oils.

In testing the color stability of gasoline to sunlight, Hoeman³⁷ used a ferric oxalate actinometer for gauging the intensity of the sunlight at the time the test exposures on the gasoline are made. Lowry, Smith and Murphy³⁸ standardized a carbon arc source against the summer sun in testing the color change in gasolines. The samples were exposed in 4-oz. oil bottles of ordinary glass, Corex glass and quartz. It was found that a West Texas gasoline, when exposed in glass to a cerium-containing carbon arc, changed in color from Saybolt 22° to 17° in ten minutes. Another listed as "commercial gasoline B" changed from 23° to 17° in thirty minutes.

A study of the way in which some gasolines become hazy and discolored and deposit sediment in a glass dispensing bowl has been made by Morrell, Benedict and Egloff.³⁹ In reviewing earlier work,⁴⁰ they state that it had been indicated that color formation in gasolines is due to oxidation reactions involving sulfur compounds or unsaturated hydrocarbons. Samples of Midcontinent straight-run gasolines, cracked gasoline and a blend of equal parts of straight-run and cracked gasoline were exposed in quartz cylinders for an hour to a carbon arc in the presence of air, oxygen, nitrogen, carbon dioxide or hydrogen. In the presence of air or oxygen, all samples developed color, gum, peroxides, acids and aldehydes. Although the straight-run and blended gasolines developed haze, the cracked ones did not. Cracked and blended gasolines developed more gum in oxygen than did

³⁴ German P. 475,343, Aug. 28, 1926, to Werschen-Weisserfeller Braunkohlen, A. G.; *Chem. Abs.*, 23, 3341 (1929). See also³².

³⁵ Kovalev, T. G., and Illarionov, V. V., *J. prakt. Chem.*, 138, 306 (1933); *Chem. Abs.*, 28, 1513 (1934).

³⁶ Panchenkov, G. M., and Puzitskii, K. W., *J. Gen. Chem. (U.S.S.R.)*, 7, 394 (1937); *Chem. Abs.*, 31, 4800 (1937).

³⁷ Hoeman, E. C., *Oil and Gas J.*, 32, No. 17, 18 (1933); *Chem. Abs.*, 27, 5525 (1933).

³⁸ Lowry, C. D., Jr., Smith, M. A., and Murphy, G. B., *Ind. Eng. Chem. (Anal. Ed.)*, 7, 140 (1935).

³⁹ Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.*, 28, 122 (1936); Egloff, G., Morrell, J. C., Benedict, W. L., and Wirth, C., *Ind. Eng. Chem.*, 27, 323 (1935).

⁴⁰ Brooks, B. T., *Ind. Eng. Chem.*, 18, 1203 (1926); Brooks, B. T., and Parker, H. O., *Petroleum*, July 14, 1924; Carpenter, J. A., *J. Inst. Petroleum Tech.*, 12, 518 (1926); *Chem. Abs.*, 21, 1702 (1927).

straight-run gasolines. Under inert gases, the straight-run gasoline dropped in color from 30° to 28° only, and the cracked and blended gasolines were unaffected. There was no formation of acid or gums and only very small amounts of peroxides.

The addition of sulfur (0.01 to 0.1 per cent) was deleterious either in the presence or absence of oxygen. With air or oxygen, it caused a marked increase in the amounts of color and gum formed. The acid formation and peroxide number were also greater than in the absence of added sulfur. With added sulfur, the color depreciation and gum formation were less in the absence of oxygen, no haze or acids appearing and only very small amounts of peroxides developing. Hydrogen sulfide was evolved in all cases. Oxygen is necessary for the formation of haze, acids or peroxides, but not always for the formation of gum or color. The elemental sulfur was almost completely removed as such during exposures either with or without oxygen. Oxides of sulfur were formed.

The addition of *n*-propyl disulfide (representative of disulfides likely to be present in gasolines or formed by sweetening) decreased the color stabilities in light and air of straight-run and blended gasolines. The decreases were greater in oxygen and even the cracked gasoline was affected. The disulfide had, however, no effect on the gum formation in gasolines exposed to air, although in those exposed to oxygen it caused a small increase. The peroxide number of the straight-run gasoline was lower and the acid number higher than in the absence of added disulfide. This was not, however, true of the cracked gasoline. Disulfide addition caused no depreciation of gasolines exposed in hydrogen, nitrogen or carbon dioxide. Mercaptans were formed during exposures in non-oxidizing atmospheres.

No fixed relation was found between color and gum formation. They can form simultaneously or gum can form with no color depreciation; or color can form without an increase in the gum content. Haze particles contain sulfur dioxide and trioxide or the corresponding acids and organic material. Most of the acid formed in gasoline was found in the haze particles which could be removed by filtration through filter paper. Although this improved the color, it did not affect the gum content of the gasoline.

Results obtained with Pennsylvania and California gasolines were similar, with the following exceptions. The Pennsylvania straight-run gasolines with no added sulfur compounds did not form gum on exposure to light and air, although gum was formed in oxygen. The addition of *n* propyl disulfide caused slight increases in gum formation in the Pennsylvania cracked gasoline and in all of the California gasolines. The results with the inert atmospheres were the same as with the Mid-continent gasolines.

These workers have again recently emphasized that color is formed only in the presence of sulfur or *n*-propyl disulfide.⁴¹

Pure hydrocarbons exposed to the carbon arc under oxygen give traces of peroxides, acids and aldehydes. The bromine number and refractive index are unchanged by light, either in the presence or absence of sulfur and propyl disulfide.⁴²

Vellinger and Radulesco⁴³ exposed samples of motor fuels under oxygen in closed Pyrex containers to the rays of a mercury lamp and found the amount of gummy material formed to be a function of the rate of absorption of oxygen. At the beginning, the quantity of gum formed was almost proportional to the amount of oxygen absorbed. Gradually, however, the absorption of oxygen diminished

⁴¹ Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.*, **28**, 122, 448 (1936).

⁴² Note also Berger, G. W., *Refiner Natural Gasoline Mfr.*, **15**, 411 (1936).

⁴³ Vellinger, E., and Radulesco, G., *Compt. rend.*, **196**, 1495 (1933); *Ann. combustibles liquides*, **8**, 883 (1933); *Chem. Abs.*, **28**, 621 (1934).

and approached a limit set by the particular pretreatment to which the sample had been subjected.

On the other hand, Freund⁴⁴ believed the absorption of oxygen of secondary importance. He considered the resins to be formed from complicated unsaturated hydrocarbons. A brief irradiation resinified only the most unstable unsaturated compounds. The resinous, gum-forming compounds produced in petroleum-cracked products by ultraviolet rays increased in amount with the exposure. Extremely small amounts were formed in comparison in primary benzenes, paraffins, naphthenes and aromatic and simple unsaturated hydrocarbons. It was found that sulfur and oxygen compounds were almost completely removed from the benzenes during separation of the resin.⁴⁵

The larger the storage tank, the slower the diffusion of oxygen and the less the gum formation. Sunlight lowers the induction period for gum formation, but water has the opposite effect. The rate of gum formation roughly triples for every twenty degrees rise in temperature.⁴⁶

To stabilize cracked distillates, especially from California or asphaltic base crudes, which contain more unsaturated and unstable constituents and more gum and coloring matter than the straight-run distillates from the same sources, Davis⁴⁷ employed a photochemical reaction. Daylight, sunlight or artificial ultraviolet sources were used and the undesirable constituents were oxidized in the presence of copper oxide. They formed organic acids which produced copper salts soluble in the oil and removed from it by subsequent distillation. A continuous stream of hydrocarbons in the vapor state mixed with oxygen can also be conveyed past a source of ultraviolet light and the oxidized products condensed, according to Martin⁴⁸.

Tauss⁴⁹ proposed to remove the resin-forming constituents in the refining of hydrocarbon oils by accelerating their polymerization by treating the hot oil or its vapor with very small amounts of oxygen and then removing the polymerization products. Other means could be used also, such as a glow discharge, irradiation or the addition of small amounts of acid or alkalis.

By a similar method, Goltstein⁵⁰ polymerized constituents in petroleum and similar hydrocarbons, thereby changing the physical characteristics of the distillate. By using an immersed quartz mercury-vapor lamp, at 60 volts and 6 amperes, the viscosity (Engler) of Russian mineral oil was increased from 6.4 to 7.8 in a half hour. The treatment may be applied to either the liquid or to the vapor phase during distillation.

In the cracking and distillation patent of Tingley,⁵¹ the oil is subjected to the action of emanations from a radioactive substance or to ultraviolet rays before it enters a conduit within the furnace of the apparatus.

Light-stability may also be increased in cracked gasoline by the addition of 0.01 to 0.5 per cent of triacetoxymethyltriethanolamine or other esters of the general formula $(\text{RCOOR}')_n\text{NH}$, in which R' is aliphatic, R aliphatic or aromatic, x is 0, 1 or 2 and n 1, 2 or 3.⁵²

Testing of Gasolines. The stability of gasolines may be tested by ultraviolet light in order to predict the tendency of the samples to form gums. Allusion

⁴⁴ Freund, M., *Brennstoff-Chem.*, **14**, 61 (1933); *Chem. Abs.*, **27**, 3808 (1933)

⁴⁵ Freund, M., see also *Proc. World's Petroleum Congress*, **2**, 108 (1933); *J. Inst. Petroleum Tech.*, **83A**, (1934); Balada, A., *Petroleum Z.*, **31**, No. 48, 11 (1933).

⁴⁶ McNamara, T. L., *Refiner and Natural Gasoline Mfr.*, **13**, 381; *Chem. Abs.*, **29**, 2721 (1935).

⁴⁷ Davis, R. F., U. S. P. 1,551,806, Sept. 1, 1925.

⁴⁸ Martin, R. B., U. S. P. 1,678,403, July 24, 1928, to Mineral Separations N. Am. Corp.; *Brit. Chem. Abs.*, **B**, 702 (1928).

⁴⁹ Tauss, J., German P. 475,277, Dec. 1, 1923; *Chem. Abs.*, **23**, 3340 (1929).

⁵⁰ Goltstein, E., British P. 249,895, Sept. 30, 1924; *Chem. Abs.*, **21**, 1007 (1927).

⁵¹ Tingley, S. L., U. S. P. 1,627,937-8, May 19, 1927; *Brit. Chem. Abs.*, **B**, 516 (1927).

⁵² Mikeska, L. A., and Holtzclaw, J. B., U. S. P. 2,110,274, March 8, 1938; *Chem. Abs.*, **32**, 3600 (1938).

to this appeared in a patent of Somerville and Hoffert.⁵³ Some have stated that the action of ultraviolet light is too severe as it resinifies certain compounds which remain stable on prolonged storage.⁵⁴ As a result the conclusions of such accelerated tests are not always in agreement with those obtained after storage for nine months. Nevertheless, the method has been frequently proposed. Beard and Reiff⁵⁵ standardize the radiations employed by their effect on an oxalic acid-uranyl acetate actinometer, and consider the effects of temperature. They note that discoloration started under radiation increases in darkness, which suggests a chain process. Schulze and Frey⁵⁶ exposed the fuel to actinic light rays while treating it with an aqueous solution of glycol and water as a separate liquid phase.

Woog, Givaudon and Dacheux⁵⁷ found that the use of white light in tests for potential gum gave unsatisfactory results. The effect of ultraviolet light was determined by exposing the sample, first in crystallizing dishes covered with Cellophane and later in Pyrex glass to a quartz mercury arc (5.4 amp., 110 volts) at about 30 cm. The results were very decisive and revealed a difference in the quality of two gasolines between which bomb tests had failed to show a difference. The tests were completed by bomb tests following the irradiation. Sufficiently reproducible results could be obtained when the gum did not exceed 10 mg. For higher values, the accuracy dropped to 10 per cent. The optimum conditions were thought to be ultraviolet treatment for one hour and heating at 100°C. for three hours. For ordinary gasoline, ultraviolet treatment for thirty minutes and heating for two hours sufficed.

Freund⁵⁸ found the results obtained by ten minutes of ultraviolet irradiation agreed closely with those of storage tests. The elementary composition of the gum so formed appeared to be the same as that formed during storage in darkness or under the influence of oxygen.

Baxter⁵⁹ observed gum formation in samples of gasoline derived from Colorado shale oil when treated in the presence of oxygen with sunlight, ultraviolet light or x-rays. Birch and Stansfield⁶⁰ found that samples of cyclohexane gave 0.2 gm. of peroxide oxygen per liter in a sample kept in light for six months and only 0.009 gm. per liter in a sample kept in darkness. No visible gum, however, deposited in the light sample. Cyclohexane in contact with air shows indications of the presence of peroxides after a short exposure to ultraviolet light.

In a patent of Rosenstein and Hund⁶¹ on the addition of selenomercaptan to produce antiknocking gasolines, it was stated that untreated gasolines containing 62.2 mg. of gum per 100 cc. had after exposure to ultraviolet light for 24 hours a gum content of 102.9 mg. per 100 cc.. Selenomercaptan-treated samples had 33.5 mg. per 100 cc. before and 33.7 mg. after a similar irradiation. It was believed that this treatment with selenomercaptan checks the tendency to gum formation and may render unnecessary any previous fixation process for the removal of unsaturated materials.

⁵³ Somerville, P. G., and Hoffert, W. H., British P. 289,347, Oct. 27, 1926; *Chem. Abs.*, **23**, 689 (1929).

⁵⁴ Brunschwig, R., *Chal. et ind.*, 315, Oct., 1928; *Brit. Chem. Abs.*, **1929B**, 931; Brunschwig, R. and Jacqué, L., *Compt. rend.*, **189**, 486 (1929).

⁵⁵ Beard, L. C., Jr., and Reiff, O. M., *Ind. Eng. Chem. (Anal. Ed.)*, **3**, 280 (1931).

⁵⁶ Schulze, W. A., and Frey, F. E., U. S. P. 1,950,697, March 12, 1934, to Philips Petroleum Co.; *Chem. Abs.*, **28**, 3562 (1934).

⁵⁷ Woog, P., Givaudon, J., and Dacheux, P., *Rev. petrolifere*, No. **584**, 721 (1934); *Chem. Abs.*, **28**, 7502 (1934).

⁵⁸ Freund, M., *World Petroleum Congress, London, Proc.* **2**, 108 (1933); *Chem. Abs.*, **28**, 4879 (1934).

⁵⁹ Baxter, R. A., *Ind. Eng. Chem.*, **21**, 1096 (1929).

⁶⁰ Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

⁶¹ Rosenstein, L., and Hund, W. J., U. S. P. 1,835,184, Dec. 8, 1931.

Lead tetraethyl in gasolines may be stabilized against light and water by a small amount of a water-soluble fluoride.⁶² One of the drawbacks to the use of iron pentacarbonyl as an antiknock agent is its instability to sunlight. Irlin and Solodovnik⁶³ propose the use of dyes as stabilizers to avoid this.

Other Applications to Petroleum Products. Chlorinated hydrocarbons for dry-cleaning, such as perchloroethylene, trichloroethylene and tetrachloroethylene, may be made stable to light by the addition of small amounts of butyl oxide, chloride or tartrate, Tetralin or Decalin.⁶⁴ Mitscherling⁶⁵ claims the formation from gasoline of alcohols and ketones by the action of a rare-gas lamp, such as one containing argon or neon. The irradiation is conducted in the presence of an oxidizing agent, such as a perborate or percarbonate, and a metal compound, such as copper hydroxide, to increase the electrical conductivity of the hydrocarbon material.

Irradiation with violet or ultraviolet light, x-rays, cathode rays, etc. has been suggested by Herbsman⁶⁶ for the separation of the components of such dispersed systems as petroleum-water emulsions or foams.

DRUGS AND RELATED PRODUCTS

There have been a few who have claimed to increase the potency of drugs by the application of ultraviolet rays. Cunningham and Macbeth⁶⁷ add fluorescent substances, such as quinine sulfate, to the liquid under treatment, vaporize it through an atomizing nozzle, and subject the vapor to the action of ultraviolet rays. Abrahamowicz⁶⁸ has proposed to treat arnica, camomile, pine needles, colts-foot, lime or elder blossoms or stinging nettles, while dry, with both x-rays and ultraviolet rays, before using them in cataplasms.

Such claims are not well substantiated. No widely used applications are known, other than to the production of vitamin D discussed in a subsequent chapter.

Instead, pharmacists have long realized that light, and particularly, the shorter wave-lengths, exerts a deleterious action upon many drug preparations. Elaborate studies, too detailed for inclusion here, on the extent to which this may occur have been conducted by Arny, Taub and Steinberg.⁶⁹ Their work was mainly directed to spectrophotometric determinations of the transmissions of various wave-lengths by the types of containers available on the American market. In general, from three to twelve times as much deterioration occurred in direct light as compared with diffused light. About 15 per cent of the drugs and chemicals tested were light-sensitive. Amber glass gave the best protection from ultraviolet rays. Red-flashed glass and Corning Red were very effective but are expensive. Few reputed stabilizers gave satisfactory results, although tin compounds stabilized phenol and, as is well known, acetanilide stabilizes hydrogen peroxide.

⁶² Michel, J. M., U. S. P. 2,067,331, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **31**, 1603 (1937).

⁶³ Irlin, A. L., and Solodovnik, *Novosti Tekhniki*, No. 26, 20 (1936); *Chem. Abs.*, **31**, 2404 (1937).

⁶⁴ de Schacken, J. M. G., and Schmidt, M. E. A., French P. 794,878, Feb. 27, 1936; *Chem. Abs.*, **30**, 5430 (1936).

⁶⁵ Mitscherling, W. O., U. S. P. 2,003,303, June 4, 1935; 2,003,898; *Chem. Abs.*, **29**, 4771, 4931 (1935).

⁶⁶ Herbsman, A. M., British P. 356,926, Aug. 27, 1930; U. S. P. 1,783,471; *Chem. Abs.*, **25**, 365 (1931).

⁶⁷ Cunningham, E. L., and Macbeth, H. F., U. S. P. 1,659,085, Feb. 14, 1928; *Chem. Abs.*, **22**, 1440 (1928).

⁶⁸ Abrahamowicz, J., British P. 455,914, 1936; *Chem. Abs.*, **31**, 2359 (1937).

⁶⁹ Arny, H. V., Taub, A., and Steinberg, A., *J. Am. Pharm. Assoc.*, **20**, 1014, 1153 (1931); *Chem. Abs.*, **26**, 1395 (1932); Arny, H. V., *Glass Packer*, **12**, 497 (1933); *Chem. Abs.*, **27**, 5913 (1933); Brunner, K., *Pharm. Zentralhalle*, **77**, 696, 721, 756, 783 (1936); Husa, W. J., *Glass Container*, **7**, No. 12, 9 (1928); *Chem. Abs.*, **23**, 236 (1929).

Eisenbrand⁷⁰ believes that for highly sensitive substances, violet manganese glass is best. For less sensitive drugs, brown iron glass will usually suffice.

Rojahn⁷¹ gave data on a number of alkaloidal solutions and tinctures. An exposure of a year to sunlight reduced the strength of tincture of hydrastis about 25 per cent and of tincture of capsicum 35 per cent. The tinctures of aconite, areca, belladonna, granatum and strophanthus were relatively stable, the losses being under 5 per cent. Alkaloidal and alkaloidal salt solutions, after 24 hours irradiation by ultraviolet light, suffered losses up to 31.3 per cent (cinchonidine). Cocaine was least affected. The losses were 23.6 per cent in tincture of hydrastis, 35.1 per cent in tincture of capsicum and 28 per cent in tincture of areca. The optical rotation also was lessened. The color of tincture of capsicum was decreased by exposure to daylight. In the tinctures of granatum, hydrastis and areca, it was increased.

Tribromoethyl alcohol is very unstable in light.⁷² An exception to the behavior of many pharmaceutical preparations is offered by the decolorized solution of iodine which, according to Merry,⁷³ should be kept in colorless glass containers exposed to sunlight.

The mydriatic action of homatropine hydrobromide is not decreased by exposure to ultraviolet light, according to Pittenger and Krantz.⁷⁴ On the other hand, Macht and Krantz,⁷⁵ found that ultraviolet rays produce a rapid deterioration of the tincture of digitalis. On prolonged exposure, a point is reached at which there are formed products of increased toxicity for both plants and animals. On further exposure, a secondary weakening in potency occurs. Ultraviolet and polarized visible light were said also to cause a decrease in the anesthetic action of some isomeric octyl alcohols.⁷⁶ Macht and Hill⁷⁷ were unable to detect any loss of the antiseptic or germicidal action of 1:500 solutions of Mercurochrome-220 after exposure to ultraviolet rays or to polarized visible light. Krantz and Carr⁷⁸ found that elixir of pepsin and rennin became less acid on irradiation, but samples stored in amber glass compared favorably after six weeks in direct light (supplemented by Alpine lamp irradiation for one-half hour each week) with fresh preparations.

The toxicity of quinine for infusoria is increased by ultraviolet irradiation of its solutions, provided the intensity is sufficient. If too great, however, the fluorescence is increased and the toxicity decreased.⁷⁹

It has been noted⁸⁰ that finely ground pyrethrum powders lose most of their toxicity in a few days of exposure to summer sunlight and air. With finely ground derris, the loss was about half as rapid. A one-hour exposure to a mercury-vapor lamp was equal in detoxicating power to eight hours of July sunlight and was

⁷⁰ Eisenbrand, J., *Pharm. Ztg.*, **72**, 1275 (1927); **74**, 263 (1929); *Chem. Abs.*, **22**, 137 (1928); **23**, 2247 (1929).

⁷¹ Rojahn, C. A., and Herzog, H., *Pharm. Zentralh.*, **73**, 401 (1932); *Chem. Abs.*, **26**, 5173 (1932); Rojahn, C. A., and Haase, E., *Pharm. Zentralh.*, **74**, 625 (1933); *Chem. Abs.*, **28**, 855 (1934).

⁷² Fialkov, Y. A., *Farm. Zhur.*, No. 3, 184 (1937); *Chem. Abs.*, **32**, 3905 (1938).

⁷³ Merry, J. J. F., *Pharm. J.*, **140**, 347 (1938); *Chem. Abs.*, **32**, 3909 (1938).

⁷⁴ Pittenger, P. S., and Krantz, J. C., Jr., *J. Am. Pharm. Assoc.*, **17**, 1081 (1928); *Chem. Abs.*, **23**, 1214 (1929).

⁷⁵ Macht, D. I., and Krantz, J. C., Jr., *Proc. Soc. Exptl. Biol. Med.*, **23**, 340 (1926); Macht, D. I., *Arch. Phys. Therapy, X-ray, Radium*, **13**, 5 (1932); *Chem. Abs.*, **26**, 1667 (1932).

⁷⁶ Schroeder, H., and Macht, D. I., *Arch. exptl. Path. Pharmacol.*, **158**, 53 (1930); *Chem. Abs.*, **25**, 4049 (1931).

⁷⁷ Macht, D. I., and Hill, J. H., *J. Am. Pharm. Assoc.*, **16**, 110 (1927).

⁷⁸ Krantz, J. C., Jr., and Carr, C. J., *J. Am. Pharm. Assoc.*, **19**, 32 (1930).

⁷⁹ Fedorov, B. T., *Bull. soc. naturalistes Moscou, Sect. biol.*, **44**, 119 (1935); *Chem. Abs.*, **30**, 2643 (1936).

⁸⁰ Badertscher, A. E., and Wotherspoon, R., *Soap (Sanitary Products Section)*, **11**, No. 4; 87, 111, 113 (1935); *Chem. Abs.*, **29**, 4125 (1935).

more constant and easily controlled. Extracts in petroleum distillates were exposed by Hoyer⁸¹ in tight flint-glass bottles to sunlight and daylight for four months and at intervals tested for their toxic action on flies. Sprays prepared with an odorless base gained slightly in toxicity during the first four days, but a sample prepared in an ordinary petroleum distillate lost toxicity from the start. After the fourth day, all samples lost toxicity rapidly, the loss being 65 per cent at two months and 90 per cent at four months. The increase observed in some at the start may have been due to the formation of an unstable toxic substance. The sprays with odorless base became hazy within three hours and their amber color was gradually lost. Finally, a white precipitate settled out. The sample with the ordinary base remained clear but lost some of its color. Chemical assays did not give consistent results. Pearson⁸² found that the substitution of some of the pyrethrum by pine oil retards some of the changes.

Fleming and Baker⁸³ found that exposure to ultraviolet light reduces the value of rotenone as a stomach poison for the Japanese beetle, although the value of derris and rotenone as repellants was but slightly reduced by exposure for 24 hours.

Prolonged sun-drying of pyrethrum caused appreciable losses, but quick drying in the sun did not.⁸⁴ According to Jones, Gersdorff, Gooden, Campbell and Sullivan,⁸⁵ the photochemical decomposition of dry rotenone does not take place in the absence of oxygen. Rotenone, its hydrochloride, rotenone-bentonite mixture, derris root and derris extract lost more than half their toxicity during a ten-day exposure to sunlight. Arc light practically destroyed their toxicity. Dihydrorotenone was more resistant, requiring twenty days in sunlight, but in arc light it lost toxicity to about the same extent as rotenone. Lampblack afforded some protection.

Anthelmintic capsules of tetrachloroethylene intended for animals, may be stabilized against light⁸⁶ by incorporating an oil-soluble red dye such as Oil Soluble Red O. Deichsel⁸⁷ uses 0.5 per cent of the azo-dye from *o*-anisidine and β -naphthol to make light-stable a solution comprising a terpene oxide such as ascaridol.

Tobacco. Ultraviolet light is occasionally applied to tobacco for the purpose of killing molds on the leaves. It has also been recommended for slightly altering the color. Dorcas⁸⁸ states that this may have important applications in foreign markets, but in the United States is not particularly important, except for leaves intended to serve as cigar wrappers. Exposure to ultraviolet also causes a number of little understood changes in the quality of the tobacco.

The Neuerburg'sche Verwaltungs Gesellschaft⁸⁹ claimed that the denicotinizing of tobacco by fermentation may be accelerated by irradiation with wave-lengths shorter than 4000Å and that the application of ultraviolet light improves tobacco which has been tainted and partly degraded by mold and other micro-organisms. Richter⁹⁰ claimed to reduce the toxicity of cut or sliced tobacco by exposing it on an endless conveyor belt to

⁸¹ Hoyer, D. G., *Soap (Sanitary Products Section)*, 11, No. 12, 105, 107, 109, 111 (1935); *Chem. Abs.*, 30, 786 (1936).

⁸² Pearson, A. M., *Del. Agr. Expt. Sta. Bull.*, 196, 5 (1935); *Chem. Abs.*, 30, 3570 (1936).

⁸³ Fleming, W. E., and Baker, F. E., *J. Agr. Research*, 53, 197 (1936); *Chem. Abs.*, 30, 8497 (1936).

⁸⁴ Beckley, V. A., and McNaughton, F., *E. African Agr. J.*, 2, 327 (1937); *Chem. Abs.*, 31, 5503 (1937).

⁸⁵ Jones, H. A., Gersdorff, W. A., Gooden, E. L., Campbell, F. L., and Sullivan, W. N., *J. Econ. Entomol.*, 26, 451 (1933); *Chem. Abs.*, 27, 4015 (1933).

⁸⁶ Anderson, C. N., U. S. P. 1,703,377, Feb. 26, 1929, to Parke Davis and Co.; *Brit. Chem. Abs.*, B, 453 (1929).

⁸⁷ Deichsel, S., U. S. P. 2,066,717, to Winthrop Chemical Co.; *Chem. Abs.*, 31, 1040 (1937).

⁸⁸ Dorcas, M. J., *Trans. Illum. Eng. Soc.*, 28, No. 7, 575 (1933).

⁸⁹ German P. 507,194 and 527,361, 1928, to Neuerburg'sche Verwaltungs Gesellschaft; *Chem. Abs.*, 25, 560, 4664 (1931). See, however, Chapter 27.

⁹⁰ Richter, C. M., *British P.* 359,920, May 3, 1929; *Chem. Abs.*, 26, 4916 (1932).

ultraviolet, infrared or visible light of specified wave-lengths. Pacini⁹¹ first dampened the tobacco with water containing a "sauce" which may contain coumarin, etc. and an agent such as glycerol, ethylene glycol, malic, or tartaric acid which was believed to counteract the opacity of the other constituents of the sauce, before irradiating it.

Lilienfield⁹² claimed the irradiation would render mild and cure, strong, previously aged and fermented tobacco leaves.

Chesley⁹³ subjects cured and aged tobacco to ultraviolet rays which constitute a selected portion of the light used. It is applied by special carbon arc lamps, the tobacco being continuously moved in a revolving drum to subject every part to the action of the rays without appreciably reducing the moisture content. There also was used a small proportion of infrared and visible radiation. Wix and Bunker⁹⁴ treat tobacco in a drum, part of the wall of which is of quartz, by a mercury arc.

In a curious method of preserving the aroma of tobacco, Senftner⁹⁵ incloses it in an envelope of cellulose material the pores of which are filled with ergosterol or cholesterol which may be irradiated.

Although the discussion (Chapter 27) of the irradiation of nicotine would indicate that the alkaloid cannot be destroyed in tobacco leaves by irradiation for a reasonable time, it has been claimed that the alkaloids in tobacco, tea, coffee, etc. may be decomposed by irradiating the products in the presence of a 1.5-per cent sodium bicarbonate solution.⁹⁶

Alcoholic Beverages. According to Henri, Helbronner and von Recklinghausen⁹⁷ wines may be quickly aged by ultraviolet irradiation. According to Petri,⁹⁸ exposure of wine to ultraviolet radiation for 0.6 to 4 seconds had no effect on the rate of fermentation, on the production of acids during maturation, or on the vitamin D content, but there may have been an insignificant increase in the content of vitamin C.

From time to time, it has been proposed to age whisky by ultraviolet light, but little or no application seems to have been made of such processes. Mancini and Archangel⁹⁹ would pass the rays into the whisky through quartz rods. The use of ultraviolet or infrared rays or a high-frequency or high-tension current in the aging of liquors is suggested by Stein¹⁰⁰ Merory¹⁰¹ irradiates the vapors during distillation.¹⁰² Philipksy¹⁰³ ages mead by irradiation. The non-aromatic constituents are removed and only the bouquet-producing extract is irradiated.

⁹¹ Pacini, A. J., U. S. P. 1,920,588, Aug. 1, 1933, *Chem. Abs.*, **27**, 4882 (1933).

⁹² Lilienfield, W. E., U. S. P. 1,731,018, 1929, *Chem. Abs.*, **23**, 5547 (1929).

⁹³ Chesley, A. L., U. S. P. 1,926,035, 1933, to American Tobacco Co.; *Chem. Abs.*, **27**, 5898 (1933); *British P.* 349,174, Feb. 21, 1930.

⁹⁴ Wix, A., and Bunker, S. W., *British P.* 421,487, Dec. 21, 1934; *Chem. Abs.*, **29**, 3786 (1935).

⁹⁵ Senftner, G., U. S. P. 1,920,483, 1933, *Chem. Abs.*, **27**, 4882 (1933).

⁹⁶ Popoff, M., *German P.* 565,373, July 6, 1929; Kennedy, D. J., U. S. P. 1,859,740, May 24, 1932 *Chem. Abs.*, **26**, 3857 (1932).

⁹⁷ Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,130,400, March 2, 1915.

⁹⁸ Petri, W., *Z. unters. Lebensm.*, **64**, 177 (1932); *Chem. Abs.*, **27**, 5469 (1933).

⁹⁹ Mancini, J., and Di Archangel, N., U. S. P. 2,040,264, 1936; *Chem. Abs.*, **30**, 4618 (1936); *Brit Chem. Abs.*, **B**, 487 (1937).

¹⁰⁰ Stein, J.-G., *German P.* 635,694, Oct. 4, 1936; *Chem. Abs.*, **31**, 805 (1937).

¹⁰¹ Merory, J., *Austrian P.* 149,188, April 10, 1937; *Chem. Abs.*, **31**, 5507 (1937).

¹⁰² For the artificial aging of wines by ultraviolet light, note also Lord Investierungs-Korporation A. G., *German P.* 638,936, Nov. 25, 1936, 652,858, Nov. 10, 1937; *French P.* 807,371, Jan. 11, 1937 *Chem. Abs.*, **31**, 3204, 5508 (1937); *British P.* 468,990, July 16, 1937. A series of sublethal exposures at long intervals is used.

¹⁰³ Philipksy, A. J. H., *German P.* 557,806, March 18, 1933; *Chem. Abs.*, **27**, 559, 4343 (1933).

MISCELLANEOUS PRODUCTS

That exposure of a polished metal surface to ultraviolet rays may render it increasingly liable to corrosion was indicated by tests conducted at the Bureau of Standards.¹⁰⁴ Specimens of Armco iron, medium carbon steel, stainless steel, and high-nickel steel were used for the test and were irradiated eight hours. Moisture from the breath condensed differently on the exposed and unexposed surfaces, rendering the two easy to distinguish. On the exposed part the drops were larger than on the unexposed part, and the surface looked as if a very thin oil film had been spread over it, making it less easily wetted than the unexposed surface. In the case of medium-carbon steels, very noticeable corrosion of the exposed spots was found to occur after four condensations of moisture, although the rest of the surface was hardly attacked. Chromium and nickel steels did not show any corrosion, although there was the same difference in appearance between the exposed and unexposed surfaces. Jameson¹⁰⁵ has described apparatus for testing the weathering properties of steel plates by exposure to water sprays and ultraviolet rays. Enos¹⁰⁶ believes ultraviolet light increases somewhat the rate of corrosion of various steels. Similar effects are probable with zinc, lead and aluminum.¹⁰⁷ In daylight or artificial light, the rate of corrosion of Electron alloy in sea water decreases with time, although in darkness it remains constant for several days.¹⁰⁸

Pfeiffer¹⁰⁹ found that the irradiation of 0.5-mm. films of asphalt on clean iron plates leads to the formation of a hard-shrinking skin formed by polymerization and oxidation. Gödrich¹¹⁰ states that ultraviolet rays render asphalt more insoluble.

Andrews¹¹¹ tests road tar by exposing a 1-mm. layer at 150°C. in a given atmosphere to ultraviolet light at 12 inches for twenty hours, with a sheet of Vita glass interposed. After this the penetration of a standard needle, 100 gm. at 5 sec., shall not be less than 50 at the temperature at which the penetration of the original sample was 100.

Neuber and Herberg¹¹² find that in petroleum asphalts, diffuse sunlight causes a shrinking of the surface layer with the formation of cracks. The oily constituents decrease with the time of exposure. The petroleum resins increase slightly, but the paraffin and ceresin content are hardly changed. The content of hard asphalt increases considerably. The nitrogen content increases considerably, but the sulfur content is unchanged. The carbon content decreases under the short ultraviolet, although it may increase under sunlight.

An accelerated testing cycle involving alternate exposure to a carbon arc and immersion in water has been described by Strieter and Snoko.¹¹³ The wash water is examined for soluble organic products. Acids and ketones are found.

Moisture in the air accelerates the changes in bituminous coatings which occur

¹⁰⁴ *Ind. Eng. Chem.*, **16**, 698 (1924).

¹⁰⁵ Jameson, C. W., *British P.* 283,539, Jan. 13, 1927.

¹⁰⁶ Enos, G. M., *Ind. Eng. Chem.*, **17**, 793 (1925); see also Bannister, C. O., and Rigby, R., *J. Iron Steel Inst.*, **133**, 293P (1936); Lavenets, I. V., *J. Applied Chem. (U.S.S.R.)*, **10**, 1556 (1937); *Chem. Abs.*, **32**, 2073 (1938).

¹⁰⁷ Bannister, C. O., and Rigby, R., *J. Inst. Metals*, **58**, 227 (1936); *Chem. Abs.*, **30**, 3390 (1936).

¹⁰⁸ Fokeev, V. M., *Vestnik Inzhenerov i Tekh.*, 302 (1933); *Chem. Abs.*, **32**, 5762 (1938).

¹⁰⁹ Pfeiffer, J. P., *Verfkroniek*, **8**, 43 (1935); *Chem. Abs.*, **29**, 4853 (1935).

¹¹⁰ Gödrich, P., *Monatsh.*, **36**, 535 (1915); *Chem. Abs.*, **9**, 3127 (1915).

¹¹¹ Andrews, R. S., *Gas J.*, **205**, 206, 259 (1934); *Chem. Abs.*, **28**, 2162 (1934).

¹¹² Neuber, F., and Herberg, E., *Mitt. tech. Versuchsanst.*, **24**, 71 (1935); *Chem. Abs.*, **30**, 4658 (1936).

¹¹³ Strieter, O. G., and Snoko, H. R., *J. Research Bureau of Standards*, **16**, 481 (1936); *Chem. Abs.*, **30**, 5326 (1936).

during exposure to 420 hours of variable sunlight. Bituminous coal-tar pitch was less affected than were blown or high-vacuum Mexican asphalt bitumen. In pure oxygen, the benzene-insoluble material of blown Mexican asphalt bitumen increased six times, although the sulfur content suffered but little change.¹¹⁴

Ried and Rusleitner¹¹⁵ find that the activity of natural or artificial fertilizers can be modified by irradiations.

The use of ultraviolet light to ionize air has been suggested as a means of removing static electricity from air in which sprays cannot be avoided.¹¹⁶ It is also mentioned by Leboucher¹¹⁷ for preventing the accumulation of charges in the manufacture of linoleum, celluloid, etc. Rathier¹¹⁸ states that static electricity can be effectively discharged from rolls of paper 750 mm. long and 600 mm. in diameter by exposing the end of the roll for ten minutes at a meter from a mercury arc. This short exposure does not affect the color of the paper. Allingham¹¹⁹ proposed to make the ionizing of air by ultraviolet light the basis of a method for partially separating the gases.

Kögel¹²⁰ in making sound records, uses gelatin and a light-sensitive organic tanning compound. The records are fixed by exposure to light.

Spectrographic Analysis. The applications of spectroscopy in industrial chemistry are so varied and the methods employing the emission spectra of the substances (elements) sought are so intricate that a discussion is not possible in a limited space. It is proving of increasing importance in metallurgy, mining, and in many other fields. A number of books and review articles are available.¹²¹ Of the 27 elements discovered since 1860, fifteen were discovered as a result of optical spectroscopy, four by x-ray spectroscopy, two by their radioactive properties and six by their chemical properties.¹²²

Analytical determinations can be made with great accuracy and a few thousandths of a milligram of metals are determinable. However, the accuracies vary from metal to metal and much experience is required for the effective handling of these methods. Histologists have adapted them to the determination of elements in definite portions of tissue sections, *e.g.*, to the determination of calcium in the various coats of the aorta.

Ultraviolet absorption spectra are being more and more widely employed both in analysis and in the study of the constitution of organic compounds. The similarity of many types of absorption spectra is, however, such that the analytical uses of the method are limited. It has been of particular importance in the development of the knowledge of the constitution of vitamins, hormones, and degra-

¹¹⁴ Walther, H., *Asphalt Teer Strassenbautech.*, 36, 1001 (1936), *Chem. Abs.*, 31, 1597 (1937).

¹¹⁵ Ried, O., and Rusleitner, K., *Austrian P.* 136,025, Dec. 27, 1933; *Chem. Abs.*, 28, 2456 (1934).

¹¹⁶ Bachhaus, A. A., *Am Dyestuff Rept.*, 16, 645, 660 (1927), *Chem. Abs.*, 22, 127 (1928).

¹¹⁷ Leboucher, P. J. M., *French P.* 675,109, Oct. 4, 1928; *Chem. Abs.*, 24, 2815 (1930).

¹¹⁸ Rathier, J., *Papier*, 37, 83 (1934); *Chem. Abs.*, 28, 2898 (1934).

¹¹⁹ Allingham, J., U. S. P. 1,553,737, Sept. 15, 1925; *J. Soc. Chem. Ind.*, 44, 904 (1925).

¹²⁰ Kögel, G., U. S. P. 2,068,919, 1937, *Chem. Abs.*, 31, 1916 (1937).

¹²¹ Gerlach, W., and Schweitzer, E., "Foundations and Methods of Chemical Analysis by Emission Spectra," London, Adam Hilger, Ltd., 123 pp., 1931.

Fitch, A. A.: "Spectrum Analysis in Mineralogy," London, Adam Hilger, Ltd., 52 pp., 1931.

Smith, D. M.: "Bibliography of Literature on Spectrum Analysis," London, British Non-ferrous Metals Research Association, 20 pp.

Crook, W. J.: "Metallurgical Spectrum Analysis," Stanford Univ. Press, 82 pp.

Gerlach, W., and Gerlach, W.: "Clinical and Pathological Applications of Spectrum Analysis, with notes on Spectrography in Chemistry and Mineralogy and Tables for Qualitative Analysis," Leipzig, L. Voss, 1933.

Owens, J. S., *Ind. Eng. Chem. (Anal. Ed.)*, 10, 64 (1938).

¹²² Eddy, C. E., *Chem. Eng. Mining Rev.*, 23, 309 (1931); *Chem. Abs.*, 25, 3918 (1931).

dation products of chlorophyll and hemoglobin. Illustrative examples of the utility of the method have been given by Fromherz.¹²³

Interesting applications have been made of emission spectrography to the study of the flames in an internal combustion engine, particularly when lead tetraethyl and other antiknocking agents are employed.¹²⁴

Fluorescence Analysis. In connection with various topics in the preceding chapters note has been made of the use of fluorescence methods for various analytical determinations. Many other applications of the use of fluorescence in filtered ultraviolet light exist and the method has stimulated a very large number of papers far too great for discussion here. Since no photochemical reactions are necessarily involved, it is unnecessary to devote space to the consideration of the details, particularly since there exist books devoted to the subject.¹²⁵ Suffice it to state that the method finds application in the study of documents for age or falsification,¹²⁶ It is also used for the detection of fraud in paintings,¹²⁷ or of the falsification of water marks in paper,¹²⁸ and for other purposes in criminology.¹²⁹ It finds varied application in industrial chemistry.¹³⁰ For example, the fluorescence of glass may be utilized in control of manufacture and in detection of the age and condition of glass.¹³¹ The so-called "natural" fluorescence has been stated to be dependent upon the physical nature of the glass as well as on its chemical properties. Also, the state of oxidation of the metal or other elements which give fluorescence to the whole was said to be an important factor. In this instance, ultraviolet light may serve as a method of control.

The characteristic fluorescence of glasses has been reported to furnish a method for identification. This was said to be particularly useful in the case of high-priced specialty glasses which sometimes are subject to fraudulent imitation. In some instances there may be introduced into the glass small proportions of substances which would render the glass highly fluorescent in ultraviolet light, without altering the properties and appearance in visible light. It is interesting to note that a fluorescence test may be employed to identify certain of the imitation glasses, such as synthetic resins.¹³²

In most of the methods proposed, the ultraviolet light source is used in a dark room in conjunction with a nickel oxide filter which transmits only the region between 3000 and 4000Å. Many substances irradiated by these wave-lengths,

¹²³ Fromherz, H., *Chem. Ztg.*, **60**, 445 (1936).

¹²⁴ Henne, A. L., and Clark, G. L., *Compt. rend.*, **184**, 26 (1927); Clark, G. L., and Thee, W. C., *Ind. Eng. Chem.*, **18**, 528 (1926); Clark, G. L., and Henne, A. L., *J. Soc. Automotive Eng.*, **20**, 264 (1927); Clark, G. L., *J. Soc. Automotive Eng.*, **23**, 167 (1928); Clark, G. L., and Smith, H. A., *J. Phys. Chem.*, **659** (1927); Rassweiler, G. M., and Withrow, L., *Ind. Eng. Chem.*, **24**, 528 (1932).

¹²⁵ Danckwortt, P. W., "Luminescenz Analyse," Leipzig, Akad. Verlags, 1934.

Bernheim, G., and Guyot, M., "Traité d'analyse par les ultraviolets filtrés." Paris, Maloine, 1932. Radley, J., and Grant, J., "Fluorescence Analysis in Ultraviolet Light." 2nd. ed., London, Chapman & Hall, 1935.

Haitinger, M., "Die Fluorescenzanalyse in der Mikrochemie." Vienna, Emil Ham & Co. Dérubère, M., "Les applications pratiques de la luminescence. Fluorescence. Phosphorescence. Lumière noire." Paris. Dunod.

¹²⁶ Kögel, G., *Sitzungsber. Preuss. Akad. Wiss.*, **37**, 97 (1914); Fonzes-Diacon, Faucon and Reynaud, *Ann. Iols.*, **17**, 20 (1924); Mellet and Bischoff, M. A., *Compt. rend.*, **181**, 868 (1925); Bonacini, C., *Brit. J. Photography*, **75**, 36 (1928); *Chem. Abs.*, **22**, 1737 (1928); Mezger, O., *Chem. Ztg.*, **53**, 965, 985, 1006 (1929); Grant, J., *Analyst*, **58**, 603 (1933); Callo, A., *British P.* 402,136 (1933); Wood, H. P., U. S. P. 2,016,474 (1935); Mitchell, C. A., *Analyst*, **58**, 532 (1933).

¹²⁷ Eihner, A., *Angew. Chem.*, **45**, 301 (1932).

¹²⁸ Grant, J., *Analyst*, **59**, 749 (1934).

¹²⁹ Mitchell, C. A., *Medical-legal Criminol. Rev.*, **3**, 3 (1935).

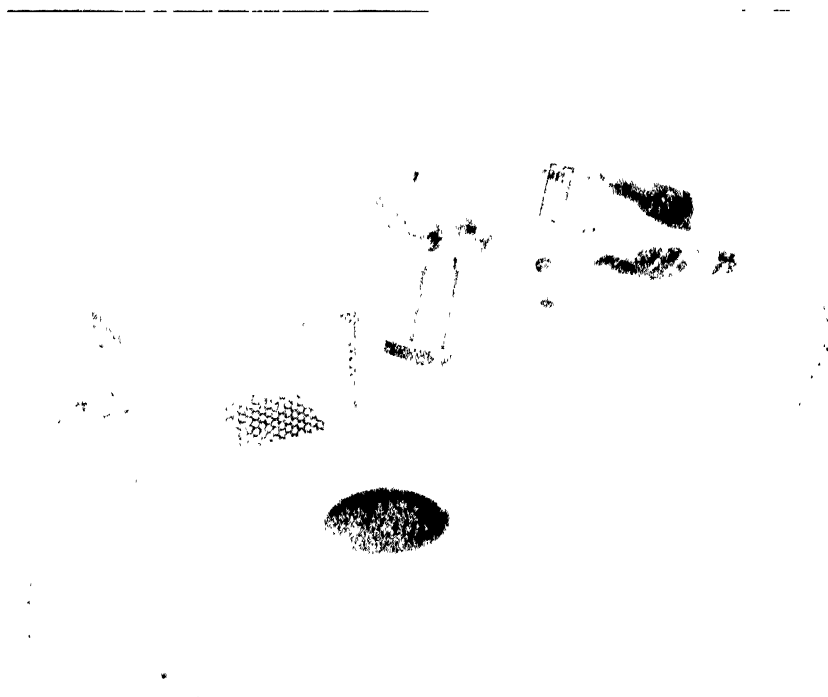
¹³⁰ Muir, J., *Ind. Chemist*, **9**, 49 (1933); Grant, J., *Ibid.*, **14**, 277, 289 (1938).

¹³¹ J. Grant, *Ceramic Industry*, 420, June, (1936).

¹³² See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

either powder, dry or in solution, exhibit characteristic fluorescence colors which, in some cases, may serve for the identification of the substances. Although minerals are well known to exhibit brilliant colors, it has been shown that various samples of the same mineral may exhibit different colors, so that the importance of the method is receding. It is, however, of value in some cases in the study of the conditions under which the mineral was originally deposited.

The method is not adapted to the identification of organic compounds by a systematic procedure. It has also been shown that many compounds which, like quinine, fluoresce brilliantly, owe this property to the presence of traces of as yet unidentified impurities. Nevertheless, there are many instances in which the method offers considerable aid in the rapid control of technical processes.



Courtesy National Carbon Co., Inc.

FIGURE 131. Eveready Fluoray Apparatus.

In Germany, there was introduced the Hanau "Quarzlampe für Analyse" as a source for this purpose. An apparatus which employs visible light, sunlight or daylight is the Callophane, merely a light-tight box for the specimen, which is illuminated by a filter of special glass on one side of the box and having provision for viewing the specimen under a black cloth thrown over the head of the observer. Figure 131 shows the Eveready carbon arc apparatus (Fluoray) devised for the purpose by the National Carbon Co. A 4-mm. Corning red-purple ultrafilter No. 587 transmits chiefly the 3650A line.

The method is extremely rapid, sensitive and does not alter the object investigated. The personal equation of the observer enters into the color readings to a considerable extent, but recently efforts have been made to adapt the method to a

quantitative recording of the intensities of the fluorescence at various wave-lengths. It is interesting to note that in a rather neglected paper, Desha¹³³ proposed a method of quantitative analysis by comparative fluorescence (fluoremetry).

Since the fluorescence of certain compounds changes with the pH of the solution in which they are dissolved, they can be employed as fluorescent indicators in titrations conducted in the light of a Wood lamp.¹³⁴

The fluorescence methods also may be adapted to microscopic objects. A fluorescence microscope was described by Haitinger and Reich.^{135, 136}

It has been proposed by Andant¹³⁷ to utilize their Raman spectra in the identification of the hydrocarbons present in gasolines.

¹³³ Desha, L. J., *J. Am. Chem. Soc.*, **42**, 1350 (1920); see also F. Bandow, *Biochem. Z.*, **295**, 154 (1938).

¹³⁴ Dérivé, M., *Documentation sci.*, **6**, 114 (1937); *Chem. Abs.*, **31**, 6086 (1937); *Tiba*, **15**, 349 (1937); *Chem. Abs.*, **32**, 1602 (1938).

¹³⁵ Haitinger, M., and Reich, V., *Chem. Fabrik*, 529, 1929; Haitinger, M., "Fluorescenzmikroskopie. Ihre Anwendung in der Histologie und Chemie." Leipzig. Akad. Verlag

¹³⁶ For a detailed discussion of modern theories of fluorescence and phosphorescence, see Pringsheim, P.; "Fluoreszenz und Phosphoreszenz im Lichte der neueren Atomtheorie," Berlin, J. Springer, 1929.

¹³⁷ Andant, A., *Chimie et industrie, Special No. 480*, June, 1933; *Chem. Abs.*, **27**, 5952 (1933).

Part IV
Biological Applications

Chapter 34

The Photochemical Behavior of Compounds of Biological Significance

An understanding of the processes underlying the biological applications of ultraviolet light demands a knowledge of the photochemical behavior of the compounds present in biological systems. Of the three chief classes of biochemical compounds—proteins, carbohydrates and lipids—the carbohydrates are discussed in Chapter 23. The fats are discussed in Chapter 29. Other lipid reactions have been relatively little studied aside from the well-known conversion of the sterols into the D vitamins. Consideration of this process is deferred to Chapter 39.

LIPIDS

Lecithin solutions, aqueous or alcoholic, absorb radiations in the region of 2970Å. Kollath¹ suggested that when skin is irradiated, its lecithin may be the source of some physiologically active substances of which acrolein may be typical. He based this upon the observation that either a very dilute aqueous solution of acrolein or an irradiated aqueous emulsion of lecithin when added to ferrous salts enabled them to aid the growth of the influenza bacillus. Kögel believes irradiation of lecithin or choline by sunlight or ultraviolet light to lessen their power of reducing a silver-metol acetic acid reagent.² In the case of lecithin, the acidity increases, because of the liberation of phosphoric and fatty acids, along with glycerol and choline.³

Although Becking and Gregersen⁴ believed the permeability of membranes made from equal proportions of collodion and lecithins to be transitorily increased by illumination, Brooks⁵ considered that this is in need of further experimental support.

The ability of cephalin to protect cholesterol sols from the coagulating action of salts is destroyed by intensive ultraviolet irradiation.⁶ An irradiated 0.25 per cent cephalin sol does not flocculate gold sols, differing in this respect from irradiated proteins. Neither does it cause the hemolysis of red blood cells, an effect which has been observed in the case of irradiated lecithin sols by Fabre and Simonnet.⁷

Bile acids no longer give the Nakagawa red reaction after ultraviolet irradiation.

¹ Kollath, W., *Klin. Wochschr.*, **6**, 13 (1927); *Chem. Abs.*, **21**, 2009 (1927); see also Spiegel-Adolf, M., *Biochem. J.*, **29**, 2413 (1935).

² Kögel, G., *Z. Krebsforsch.*, **46**, 105 (1937); *Chem. Abs.*, **31**, 8670 (1937).

³ Roffo, A., and Correa, L., *Bol. inst. med. exptl. No 42* (1936); *Rev. sudamericana endocrinol. immunol. quimiotherap.*, **20**, 548; *Chem. Abs.*, **32**, 201 (1938).

⁴ Becking, B. L., and Gregersen, M., *Proc. Soc. Exptl. Biol. Med.*, **22**, 130 (1924); *Chem. Abs.*, **19**, 3273 (1925).

⁵ Brooks, S. C., *Science*, **61**, 214 (1925). See also Brauner, L., and Brauner, M., *Protoplasma*, **28**, 230 (1937).

⁶ Spiegel-Adolf, M., *J. Am. Chem. Soc.*, **57**, 1431 (1935).

⁷ Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10**, 1036 (1928); *Chem. Abs.*, **24**, 1126 (1930)

tion.⁸ Such treatment also reduces the ability of sodium glycocholate to detoxify certain organ poisons (lung or intestine).⁹

On irradiation, methyl cholate in chloroform becomes yellow, shows a decreased rotation, and yields on fractional crystallization, a β -ester of lower rotation and higher melting point. A stereoisomeric change is believed to occur at the secondary hydroxyl group of ring III of the ester. Neither the free acid nor its sodium salt in water suffered the isomerization. The β -ester differed from the original α -form in its greatly retarded Mylius reaction, its greater solubility, and its failure to be precipitated by digitonin. A further product of the irradiation was a resin which on saponification yielded a yellow acid, $[\alpha]_D^{20}=25$, with a titration equivalent of 591.7, and probably a condensation product of cholic acid.^{10, 11}

PROTEINS AND AMINO-ACIDS

The photochemistry of the proteins is best approached by considering first the behavior of their degradation products, the amino-acids. The absorption of ultraviolet light by proteins is very largely due to their ring-containing amino-acids, tryptophane, phenylalanine and tyrosine.¹² These amino-acids exhibit selective absorption between about 2400 and 2900A, the maximum being at about 2750A, at least in the case of tryptophane.¹³ In connection with other investigations, Svedberg and co-workers have given ultraviolet absorption curves for a number of proteins, from which it can be readily shown that the selective absorption with maximum at 2750 to 2800A depends in large part upon the content in the proteins of the amino-acids tryptophane and tyrosine. The influence of most of the remaining amino-acids is evident chiefly in the absorption at wave-lengths of 2300A or less. Of recent years many papers,¹⁴ on details of the absorption spectra of proteins have appeared.¹⁵

Amino-Acids. Tryptophane and tyrosine are sensitive to irradiation with ultraviolet light, absorbing oxygen under its influence. This accounts for most of the oxygen uptake by irradiated plasma, according to Harris.¹⁶

⁸ Mikami, H., *J. Biochem. Japan*, **14**, 489 (1932); *Chem. Abs.*, **26**, 1968 (1932).

⁹ Ito, R., *Folia Pharmacol. Japan.*, **12**, No. 2, 131 (1931); *Chem. Abs.*, **25**, 5507 (1931).

¹⁰ Uraki, Z., *Z. physiol. Chem.*, **207**, 16 (1932); *Chem. Abs.*, **26**, 3802 (1932).

¹¹ Phosphatides and other lipids are irradiated in a patent of "Pharmagans" Farm. Ins. L. W. Gans, A. G., Kollath, W., and Magistris, H., *British P.* 311,436, Jan. 10, 1928; *Chem. Abs.*, **24**, 920 (1930).

¹² Harris, F. L., and Hoyt, H. S., *Pathology*, **2**, 245 (1919); *Chem. Abs.*, **13**, 2384 (1919).

¹³ Holiday, E. R., *Biochem. J.*, **30**, 1795 (1936); Feraud, K., Dunn, M. S., and Kaplan, J., *J. Biol. Chem.*, **112**, 323 (1935); **114**, 665 (1936); Heidt, L. J., *J. Biol. Chem.*, **115**, 223 (1936). These references give extensive citations to earlier work.

¹⁴ Shibata, Y., and Asahina, T., *Bull. Chem. Soc. Japan*, **1**, 71 (1926); **2**, 324 (1927); Grinbaum, R., and Marchlewski, L., *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **A**, 156 (1937); *Chem. Abs.*, **32**, 1576 (1938).

¹⁵ Some of the more important are the following: Abderhalden, E., and Haas, R., *Z. physiol. Chem.*, **155**, 195 (1926); Gioh, G., and Weltner, M., *Ibid.*, **198**, 267 (1931); Vies, F., and Prager, M., *Arch. Phys. Biol.*, **10**, 5 (1932); *Chem. Abs.*, **27**, 5643 (1933); Roche, J., and Dubouloz, P., *Compt. rend.*, **196**, 646 (1933); Marchlewski, L., and Wierzechowska, J., *Bull. Acad. Polonaise*, **A**, 471 (1928); *Brit. Chem. Abs.*, **A**, 459 (1929); Theorell, H., *Biochem. Z.*, **268**, 55 (1934); Giza, T., *Bull. Intern. Acad. Polonaise*, **A**, 421 (1934); *Chem. Abs.*, **29**, 2977 (1935); Porcher, C., Volklinger, H., and Brigando, J., *Lait*, **14**, 1041 (1934); *Chem. Abs.*, **29**, 3697 (1935); Hicks, C. S., and Holden, H. F., *Australian J. Exp. Biol. Med. Sci.*, **12**, 91 (1934); *Chem. Abs.*, **29**, 2556 (1935); Coulter, C. B., Kabat, E. A., and Stone, F. M., *J. Bacteriol.*, **29**, 54 (1935); *J. Gen. Physiol.*, **19**, 739 (1936); Grinstein, M., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires)*, **7**, 351 (1936); Mitra, B. N., *Indian J. Med. Research*, **24**, 5 (1936); Almquist, H. J., Givens, J. W., and Klose, A., *Ind. Eng. Chem.*, **26**, 847 (1934); Gioh, J., and Faltin, E., *Z. physiol. Chem.*, **199**, 13 (1931); Gioh, J., and Weltner, M., *Biochem. Z.*, **273**, 389 (1934); Freudenberg, K., Discherl, W., and Eyer, H., *Z. physiol. Chem.*, **187**, 89 (1930); Vies, F., and Cohn, C., *Arch. Phys. Biol.*, **5**, 48 (1926); *Chem. Abs.*, **21**, 2997 (1927); DeBoer, J. H., Dippel, C. J., and Custers, J. F. H., *Rec. trav. chim.*, **52**, 195 (1933); Smith, F. C., *Proc. Roy. Soc.*, **104B**, 198 (1929); Asahina, T., *Bull. Chem. Soc. Japan*, **4**, 202 (1929); **5**, 354 (1930). For a collection of over two hundred curves for the absorption of proteins, carbohydrates and fats, see Ellinger, F., *Tabulae Biologicae*, **12**, 291 (1937).

¹⁶ Harris, D. T., *Biochem. J.*, **20**, 288 (1926).

Berthelot and Amoreux find tryptophane forms indole-3-acetic acid, detectable after ten minutes of mercury arc irradiation of a solution of 0.5 gm. per liter in a quartz flask. The change is retarded by acidification to pH 4.5.¹⁷

The non-aromatic amino- acids, such as glycine, alanine, valine, leucine, and aspartic acid, either do not show an increased rate of oxidation when irradiated, or show it less readily. Lieben¹⁸ found that sensitizers such as hematoporphyrin increase the oxygen absorption of the aromatic amino- acids in the light of the quartz lamp and even enable them to show some activity in, diffused daylight. The velocity of the oxidation is increased by alkalinity and, in the case of tryptophane, by the addition of formaldehyde. When combined in proteins, the destruction of these amino- acids by light is retarded. They are of particular interest because of their possible participation in the mechanism by which the pigment melanin, or a related substance, may be formed during tanning by sunlight.

Arnow¹⁹ finds irradiation to convert *l*-tyrosine into *dopa* (*l*-3,4-dihydroxy-phenylalanine), which itself can be destroyed by prolonged irradiation. An oxidase of certain skin cells (the melanoblasts) converts *dopa* into the tan pigment melanin.

The absorption spectra of the aliphatic amino- acids have been interpreted as indicative of a zwitterion structure $^+\text{NH}_3\text{CH}_2\text{COO}^-$.²⁰

The wave-length at which the continuous absorption of the glycine cation, $\text{NH}_3^+\text{CH}_2\text{COOH}$ begins has been considered by Onslow, Foster and Klingler²¹ to afford a measure of the energy required for its dissociation into a hydrogen ion and the zwitterion $\text{NH}_3^+\cdot\text{CH}_2\cdot\text{COO}^-$. In water, it begins at the wave-number 51894 and in hydrochloric acid at 51813, corresponding to 146.86 and 146.63 kcal., respectively. The dissociation frequency is regarded as the sum of the limiting frequency of the Balmer series for hydrogen and of a natural vibration frequency of the molecule-ion, the latter term varying in different amino- acids inversely as the square root of the molecular weight of the zwitterion. In alkaline solution, the glycine cation exists as $\text{NH}_3^+\text{CH}_2\text{COONa}$. Dissociation occurs at a wave-number corresponding to 138.59 kcal. Irradiation with ultraviolet light causes polymerization.

After irradiation by a mercury arc for fifteen hours, a 0.1*N* aqueous glycine solution increased in conductivity from 1.54×10^{-5} to 71.20×10^{-5} . Its pH increased from 4.8 to 7.45. These changes are due to the formation of ammonia as a result of hydrolysis;



Glycolic acid, but no acetic acid, was formed and the occurrence of side reactions was indicated by the evolution of a gas rich in carbon monoxide. The reaction was most rapid, according to Henri, Weismann and Hirschberg,²² at pH 3, declining with increasing pH to a minimum at pH 6 and then increasing slowly. Although the absorption begins at about 2400Å, wave-lengths less than 2205Å are required to produce the decomposition. The quantum yields are about 0.09 for glycine, 0.1 for alanine, and 0.06 for the compound betaine. The rate of reaction is much greater in alanyl-glycine than in glycine and in phenylalanine than in alanine.²³

¹⁷ Berthelot, A., and Amoreux, G., *Compt. rend.*, **206**, 699 (1938).

¹⁸ Lieben, F., *Biochem. Z.*, **184**, 453 (1927).

¹⁹ Arnow, L. E., *J. Biol. Chem.*, **120**, 151 (1937); *J. Phys. Chem.*, **42**, 415 (1938).

²⁰ Ley, H., and Zachacke, F. H., *Ber.*, **57B**, 1700 (1924); Leuthardt, F., and Pfister, M., *Helv. Chim. Acta*, **16**, 228 (1933); Ueda, H., *J. Chem. Soc. Japan*, **50**, 502 (1929); *Chem. Abs.*, **26**, 91 (1932); Ley, H., and Arends, B., *Ber.*, **61B**, 212 (1928).

²¹ Onslow, G. A., Foster, M. L., and Klingler, C., *J. Biol. Chem.*, **103**, 81 (1933).

²² Henri, V., Weismann, C., and Hirschberg, Y., *Compt. rend.*, **198**, 168 (1934); **199**, 1205 (1935).

²³ Weismann, C., Hirschberg, Y., and Bergmann, E., *J. Am. Chem. Soc.*, **60**, 1799 (1938).

Aspartic acid also is hydrolyzed by ultraviolet light.²⁴ Irradiation of *l*-aspartic acid produces a new absorption band at 2650Å, according to Becker,²⁵ which is not observed in the case of either asparagine or malic or tartaric acids. Becker showed later that both *l*-aspartic acid and *l*-asparagine yield acetaldehyde upon irradiation. The decomposition products of glycylglycine are different. Because of their α -hydroxyl groups, *dl*-serine and *dl*-lactic acid react differently from *dl*-alanine.²⁶

The splitting of ammonia from amino-acids as a result of irradiation has also been studied by Lieben and Urban;²⁷ only the α -amino-group undergoes this reaction. It is greatest in histidine, 88 per cent, and next in cystine, 32.7 per cent. It is twice as great in lysine, 20.9 per cent, as in arginine, 9.4 per cent. The total decomposition of histidine, tyrosine, or tryptophane, as measured colorimetrically, did not agree with the amount of ammonia evolved, indicating the occurrence of secondary reactions, as had been suggested by Weizmann in the case of glycine. Guanidine was resistant and did not evolve ammonia when irradiated. The amino-group in guanine or in anthranilic acid or benzdine is displaced as easily as when it is present in a side chain.

Hippuric acid is very stable in sunlight.²⁸ The irradiation of hydroxyproline solutions by a quartz lamp produces two new absorption bands at 2570 and 3130Å; the latter does not appear if the solid is irradiated.²⁹

Ellinger³⁰ found that irradiation of a 1-per cent solution of histidine hydrochloride by a quartz mercury arc yields traces of a decomposition product detected pharmacologically by its histamine-like action. Histamine is the product of the decarboxylation of histidine. Photocatalysts did not accelerate the rate of the conversion, which, within certain limits, was unaffected by the pH of the solution or by the duration of the irradiation. Further application of radiations of the wavelengths 2970 and 3020Å caused a loss of the pharmacological activity of the irradiated solutions. During the irradiation of histidine, changes in the absorption spectra, interpreted as indicative of the decarboxylation of histidine,³¹ were observed. Becker,³² however, pointed out that the similarity of the absorption spectra of histidine and of histamine is such that the optical method is unsuited for following the decarboxylation of histidine. Ellinger³³ later admitted that what he had regarded as the characteristic absorption of histidine hydrochloride in the longer wave-length region of the ultraviolet had been due to the presence of traces of iron compounds as impurities.

Nevertheless, renewed interest in the reaction was aroused by the demonstration by Holtz³⁴ that histamine is produced by the irradiation of a 1:150 solution of histidine at pH 12 in the absence of oxygen. He was able to isolate 7 mg. of histamine, identified by melting point and analysis of the crystalline pictrate, chloroaurate and chloroplatinate, from the products of irradiation of 1 gm. of histidine.

²⁴ Weizmann, C., Bergmann, E., and Hirschberg, Y., *Ibid*, **58**, 1675 (1936).

²⁵ Becker, J. P., *Strahlentherapie*, **50**, 357 (1934), *Chem. Abs.*, **28**, 5338 (1934).

²⁶ Becker, J. P., *Strahlentherapie*, **52**, 531-537 (1935); *Brit. Chem. Abs.*, **A**, 437 (1936).

²⁷ Lieben, F., and Urban, F. F., *Biochem. Z.*, **239**, 250 (1931), *Oesterr. Chem. Ztg.*, **37**, 20 (1934).

²⁸ Enseline, J., and Pozzi, M., *Bull. soc. chim. biol.*, **17**, 283 (1935).

²⁹ Becker, J. P., *Strahlentherapie*, **48**, 296 (1933); *Chem. Abs.*, **28**, 1064 (1934).

³⁰ Ellinger, F., *Archiv exp. Path. Pharmacol.*, **136**, 129 (1928).

³¹ Ellinger, F., *Biochem. Z.*, **215**, 279 (1929).

³² Becker, J. P., *Arch. ges. Physiol. (Pflügers)*, **228**, 751 (1931).

³³ Ellinger, F., *Biochem. Z.*, **248**, 437 (1932).

³⁴ Holtz, P., *Klin. Wochschr.*, **12**, 1613 (1933); *Archiv exp. Path. Pharmacol.*, **175**, 97 (1934).

Ellinger³⁵ had not been able to identify the irradiation products chemically or spectroscopically after the irradiation of histidine, dry or in solution, but observed that the irradiated solution excites the intestine of a guinea pig. The extracts made with hot chloroform also lowered the blood pressure. Since the injection of histamine into the skin is known to lead to the production of an erythema, Ellinger suggested that the erythema of sunburn may be due to the production of a histamine-like substance from histidine in the upper layers of the epidermis. It was possible to obtain considerable amounts of such substances from even the non-irradiated skin of guinea pigs, although such extracts were never more active than those of irradiated samples.

Szendrő³⁶ maintains that imidazoleacetaldehyde is the material formed in the irradiation of histidine. On the other hand, according to Wrede and Holtz,³⁷ the irradiation of imidazoleethyl alcohol does not yield depressor substances.

The oxidation of cystine is not induced by irradiation, according to Harris,²⁸ and cysteine takes up oxygen so rapidly in darkness that any acceleration produced by ultraviolet light is negligible in comparison with that produced in the case of tryptophane or tyrosine.

The energy required for the dissociation of cystine in hydrochloric acid solutions is, from the absorption spectrum, 70.8 kcal.³⁸ Lieben and Molnar,⁴⁰ find that, although both cystine and cysteine do decompose under the quartz mercury arc, the process proceeds much more slowly than in the case of the aromatic amino-acids. In diffused daylight, the destruction of cystine occurs only in an alkaline medium. Since cysteine oxidizes spontaneously in an alkaline solution, its behavior must be studied in an acid medium and for this a photosensitizer, such as hematoporphyrin, is required in daylight. In the arc light, however, there is a slow decomposition in the absence of a sensitizer. Szendrő, Lambert and Wrede⁴¹ claim that *l*-cysteine is formed in 5-per cent yields when cystine is irradiated with ultraviolet light.

Rao and Dhar⁴² studied the photo-oxidation of amino-acids in sunlight in the presence of such sensitizers as titanium dioxide, zinc oxide and alumina. The products formed from the aliphatic representatives included aldehydes, carbon dioxide and ammonia. Monoaminodicarboxylic acids acted less readily than the monoaminomonocarboxylic acids. Anthranilic acid gave aniline and carbon dioxide. Ort has given some attention to the catalytic influence which amino-acids may exert upon the oxidation of sugars irradiated in the presence of hydrogen peroxide.⁴³

It is apparent from a consideration of the observations recorded in these paragraphs that, although a quartz mercury arc produces certain changes in amino-acids, the radiations available in sunlight or even from artificial sources under the usual conditions of their therapeutic applications, are incapable of affecting the amino-acids other than those which contain an aromatic, indole or imidazole ring.

³⁵ Ellinger, F., *Archiv exp. Path. Pharmacol.*, **153**, 120 (1930); *Strahlentherapie*, **38**, 521 (1930); *Chem. Abs.*, **25**, 526 (1931).

³⁶ Szendrő, P., *Arch. ges. Physiol. (Pflüger's)*, **228**, 743 (1931); *Chem. Abs.*, **26**, 1862 (1932).

³⁷ Wrede, F., and Holtz, P., *Arch. ges. Physiol. (Pflüger's)*, **234**, 432 (1934); *Chem. Abs.*, **28**, 5477 (1936).

³⁸ Harris, D. T., *Biochem. J.*, **20**, 288 (1926).

³⁹ Foster, M. L., Anslow, G. A., and Barnés, D., *J. Biol. Chem.*, **89**, 665 (1930); Barnés, D., *Anales Soc. Espan. Fis. Quim.*, **28**, 1386 (1930); *Chem. Abs.*, **25**, 2366 (1931).

⁴⁰ Lieben, F., and Molnar, F., *Biochem. Z.*, **230**, 347 (1931).

⁴¹ Szendrő, P., Lambert, V., and Wrede, F., *Z. physiol. Chem.*, **222**, 16 (1933).

⁴² Rao, G. G., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 617 (1934); *Chem. Abs.*, **29**, 1326 (1935).

⁴³ Ort, J. M., *J. Phys. Chem.*, **33**, 825 (1929).

In general, there is, on the irradiation of amino-acids with light of sufficiently short wave-length, an evolution of ammonia and a shift of the absorption spectrum to somewhat longer wave-lengths.⁴⁴

The optical rotations of optically active dipeptides are unaltered by exposure to ultraviolet light, but solutions of the corresponding 2,5-diketopiperazines show a diminution in rotation which soon reaches a constant value. Traces of ammonia and carbon dioxide can be detected after irradiation in air, but not in nitrogen, so that the mechanism probably involves oxidation. Solutions of silk peptones show similarly altered rotations.⁴⁵

The irradiation of a solution of Witte's peptone produces a skin on the surface. This skin fails to give the biuret reaction. The tyrosine content is reduced, as is that of histidine and there is no tryptophane present. Since the amino-nitrogen content in this skin is found to be reduced, it is probable that the production of plasteins may have occurred. The minimum amount of skin is formed at pH 5.5. On removal of the film, a new one forms on further irradiation. Solutions of the peptones from casein or silk fail to behave in a similar manner.⁴⁶

Behavior of Proteins on Irradiation.⁴⁷ In 1913, Bovie⁴⁸ reported that fresh egg albumin, on exposure in a quartz tube at 10 cm. from a mercury arc lamp at room temperature, began to show a feathery coagulum on the walls nearest the lamp and after 35 hours had become fully coagulated and possessed a peculiar, strong odor. When an aqueous solution was employed, less time was required for the coagulation. The product formed settled to the bottom of the tube. Crystalline albumin not freed from ammonium sulfate coagulated more rapidly than fresh egg-white. After dialyzing away the salt, the protein was still more sensitive and showed some coagulation even when exposed in glass tubes. Ox-serum was also coagulated in quartz tubes. No coagulation occurred at zero, but if the solution was then warmed a few degrees it became turbid. If the temperature was then quickly reduced, the solution again became clear. It was suggested that light alters the protein at low temperatures, but that only at higher temperatures does there occur a second change leading to the production of a visible coagulum.⁴⁹

Many observations have since been made of the phenomenon. In the case of serum albumin, Teichler,⁵⁰ believed the coagulating action, although not the primary photochemical process, to be dependent upon the relative amounts of sodium and calcium ions present.

The question has been frequently raised as to whether the mechanism is the same as that of the coagulation by heat. Bovie believed this to be the case, since he found the coagulated material soluble in dilute alkali, but insoluble in alcohol, water or dilute acid. Spiegel-Adolf and Krumpel⁵¹ found that the absorption spectrum changes during heat coagulation in a manner similar to that during

⁴⁴ Allen, A. J., Steiger, R. E., Magill, M. A., and Franklin, R. G., *Biochem. J.*, **31**, 195 (1937); Magill, M. A., Steiger, R. E., and Allen, A. J., *Biochem. J.*, **31**, 188 (1937).

⁴⁵ Abderhalden, E., and Haas, R., *Z. physiol. Chem.*, **155**, 195, 200 (1926); **166**, 78 (1927); **160**, 256 (1926); **164**, 1 (1927); Hünecke, H., *Ber.*, **60B**, 1451 (1927); Ley, H., and Arends, B., *Ber.*, **61B**, 212 (1928); Abderhalden, E., and Rossner, E., *Z. physiol. Chem.*, **176**, 249 (1928); **178**, 156 (1928); Asahina, T., *Bull. Chem. Soc. Japan*, **4**, 202 (1929); Guthmann, H., Schwerin, K., and Stähler, F., *Strahlentherapie*, **39**, 401 (1931); *Chem. Abs.*, **25**, 2448 (1931).

⁴⁶ Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).

⁴⁷ This subject has been reviewed in considerable detail by Arnow, L. E., *Physiol. Revs.*, **16**, 671 (1936).

⁴⁸ Bovie, W. T., *Science*, **24**, 374 (1913).

⁴⁹ Bovie, W. T., and Hughes, D. M., *J. Gen. Physiol.*, **1**, 323 (1919); Bovie, W. T., and Klein, A., *Ibid.*, **1**, 331 (1919); Bovie and Daland, G. A., *Am. J. Physiol.*, **66**, 55 (1923).

⁵⁰ Teichler, G., *Arch. ges. Physiol. (Pflüger's)*, **227**, 558 (1931); *Chem. Abs.*, **25**, 4289 (1937).

⁵¹ Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **208**, 45 (1929).

irradiation, but that the changes were quantitatively less in the former case. However, Spiegel-Adolf found also, at least in the case of serum albumin,⁵² that the coagulum formed by irradiation differed from that formed by heat in not being rendered water-soluble by dilute alkali followed by dialysis. After irradiation in the presence of hydrochloric acid, serum albumin can be salted out, but this differs from the behavior on heating in the presence of acid. In spite of these differences, serum albumin heated or irradiated in the presence of sodium hydroxide shows the same behavior to neutral salts. The presence of larger concentrations of neutral salts does not prevent the coagulation of serum albumin during irradiation, but the presence of multivalent ions does inhibit the precipitation. Potassium thiocyanate does not inhibit the irradiation coagulation and cannot bring the product into solution, differing in this respect from its effects on heat coagulation.

Clark⁵³ pointed out that only at pH values near the isoelectric point is albumin coagulated by either light or heat. At other pH values, it remains clear on irradiation but has been altered by the process so that it behaves toward electrolytes as a globulin. Other workers, notably Abderhalden, observed that a slight decrease in pH occurs during the irradiation of globulin and, in the presence of sodium chloride, albumin solutions. The optical rotation also decreases, but the conductivity increases slightly. The increase in acidity was also observed by Mond,⁵⁴ who found the viscosity increased, and the surface tension decreased. The latter effect was less in the case of albumin than of globulin.⁵⁵

Stedman and Mendel⁵⁶ extended the investigations to about twelve purified proteins. In general, there was a lowering of the coagulation temperature, together with the production of an odor and a yellow tint, and in some cases, an increase in the specific rotation. These changes were independent of the presence of water, electrolytes and oxygen. In tests of some fourteen proteins, it was found by Spiegel-Adolf and Pollaczek⁵⁷ that bacterial contamination of the solutions retarded their coagulation during irradiation. The retarding effect persisted even after the infection had spontaneously died.

Rajewsky⁵⁸ found the primary denaturation process independent of temperature, only the conglomeration of the denatured particles being accelerated by a rise in temperature. Gentner and Schwerin⁵⁹ followed the coagulation by following the changes in the number of particles exhibiting Brownian movement. At the isoelectric point of egg albumin, three processes rather than two may be recognized as involved in the mechanism of coagulation, according to Clark.⁶⁰ Following the primary photo-denaturation, she believes there ensues a reaction between the denatured molecule and water, following which there is a flocculation of the denatured molecules to form the coagulum. The first denaturation is a monomolecular process, which, in agreement with Rajewsky, is independent of temperature. The reaction with water has, however, a high temperature coefficient—over ten. The reaction occurs rapidly at 40°C., a temperature at which heat denatura-

⁵² Spiegel-Adolf, M., *Biochem. Z.*, **186**, 181 (1927).

⁵³ Clark, J., *Am. J. Physiol.*, **73**, 649 (1925).

⁵⁴ Mond, R., *Arch. ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J. Chem. Soc.*, **123**, and **124**, (1), 868.

⁵⁵ Other early observations of this type were due to Schanz, F., *Archiv ges. Physiol. (Pflüger's)*, **164**, 445 (1916); *Chem. Zentr.*, **87**, II, 670 (1916); *Chem. Abs.*, **10**, 1656 (1916), and to Kreibich, C., *Arch. Path. Anat.*, **222**, 28 (1916); *Chem. Abs.*, **14**, 2023 (1920).

⁵⁶ Stedman, H. L., and Mendel, L. B., *Am. J. Physiol.*, **77**, 199 (1926).

⁵⁷ Spiegel-Adolf, M., and Pollaczek, K. F., *Biochem. Z.*, **214**, 175 (1929).

⁵⁸ Rajewsky, B., *Biochem. Z.*, **227**, 372 (1930); *Klin. Wochschr.*, **10**, 1673 (1931).

⁵⁹ Gentner, W., and Schwerin, K., *Biochem. Z.*, **227**, 286 (1930).

⁶⁰ Clark, J., *J. Gen. Physiol.*, **19**, 199 (1935).

tion is inappreciable. Mirsky and Pauling⁶¹ suggest that the primary absorption process causes a break in the native protein molecule which enables it to suffer denaturation at a temperature lower than that otherwise required.

Little is known as yet of the precise nature of this primary process. Lampert and Wels⁶² noted during irradiation in the absence of oxygen the formation of a substance with sulphydril reactions which cannot, however, be separated from the proteins by ultrafiltration or by precipitating the protein with colloidal ferric hydroxide. Mirsky and Anson⁶³ observed that the number of sulphydril groups in egg albumin coagulated by ultraviolet light is equivalent to that in samples coagulated by typical denaturing agents.

Other observations of chemical decompositions involved have been occasionally made. Hoffmeister⁶⁴ claims that after five hours of irradiation of serum albumin and peptone, the values for acetaldehyde were as high as 68 and 108 mg., respectively, as compared with 18 and 8 mg. in non-irradiated controls. Howitt⁶⁵ also suggested that formaldehyde or some similar substance is produced from egg albumin, and that this, by reacting with amino- groups, might account for an observed increased acidity. An alkaline reaction favors the last step and tends to lessen the possibility of a reducing action by the aldehyde.

Gelatin and globin (and also the alkaloid caffeine), when irradiated in weakly acid solutions, yield ammonia, according to Eckstein and Lieben.⁶⁶ These observers do not believe an increase in amino- nitrogen to be due to a cleavage of peptide linkages, since peptides are not hydrolyzed under these conditions. They also exclude arginine as the source and believe that both the ammonia and the increased amino-nitrogen originate from the heterocyclic rings of histidine, proline and hydroxyproline. Lieben and Jesserer,⁶⁷ however, admit that the peptide linkages in proteins may be less resistant than they are in peptones and peptides, so that it may not be necessary to conclude that the origin is exclusively the breaking of heterocyclic rings.

Much attention has been devoted to the changes wrought by irradiation in the colloidal behavior of the proteins. Mond⁶⁸ believed that the stability of solutions of serum globulin and fibrinogen are increased since their coagulation temperatures were raised.

According to Cossu,⁶⁹ non-irradiated samples of serum albumin show a minimum in the surface tension-pH curve at the isoelectric point, but after irradiation there is a maximum at the isoelectric point and another at a point on the acid side. The protein is no longer stable at the isoelectric point as shown by the fact that the solutions are slightly turbid.

Monomolecular albumin films on irradiation dissolve completely in about two hours.⁷⁰ Mitchell⁷¹ found that the phase-boundary potentials of egg albumin films increase when irradiated by the 2537Å line. The solid film liquefies. It was sug-

⁶¹ Mirsky, A. E., and Pauling, L., *Proc. Nat. Acad. Sci.*, **22**, 439 (1936).

⁶² Lampert, U., and Wels, P., *Archiv exp. Path. Pharmacol.*, **175**, 554 (1934).

⁶³ Mirsky, A. E., and Anson, M. L., *J. Gen. Physiol.*, **19**, 427 (1936). See also Wenig, K., and Jirovec, O., *Biochem. Z.*, **295**, 405 (1938).

⁶⁴ Hoffmeister, A., *Z. physiol. Chem.*, **205**, 183 (1932).

⁶⁵ Howitt, F. O., *Nature*, **125**, 412 (1930).

⁶⁶ Eckstein, H. C., and Lieben, F., *Biochem. Z.*, **263**, 366 (1933).

⁶⁷ Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).

⁶⁸ Mond, R., *Archiv ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J. Chem. Soc.*, **123-4**, 868 (1923).

⁶⁹ Cossu, F., *Bull. soc. ital. biol. sper.*, **10**, 973 (1935), *Chem. Abs.*, **30**, 2589 (1936).

⁷⁰ Rideal, E. K., *Kolloid-Z.*, **61**, 218 (1932).

⁷¹ Mitchell, J. S., *Proc. Roy. Soc.*, **A155**, 696 (1936).

gested that certain CO—NH linkages in the main polypeptide film may be hydrolyzed. It could be shown that this linkage is broken in stearic anilide to the extent of at least 95 per cent, the quantum yield being unity, but varying with the molecular orientation in a manner for which a theory was given. Mitchell called attention to the interesting possibilities offered in biological work by the fact that the photochemistry of monomolecular layers offers a means of studying the effects of orientational factors.

Among the most carefully conducted and detailed studies of the changes occurring in proteins are those of Spiegel-Adolf.⁷² With Krumpel,⁷³ she showed irradiation to increase the ultraviolet absorption of solutions of electrolyte-free serum albumin in the region 4000 to 2675 Å, without affecting the location of the absorption maxima and minima. Oxygen was not necessarily present in order to produce these changes. Pseudo-globulin and serum itself also exhibit an increase in absorption when irradiated in the presence of alkali, but euglobulin does not. Egg albumin behaves as does serum albumin.⁷⁴ If acid or alkali is added before the irradiation, the increase in absorption increases with the concentration of the added acid or alkali. The effects are much less marked when x-ray or radium irradiation is employed. However, in the presence of materials which under x-radiation fluoresce in the ultraviolet region, the effects of x-rays are similar to those of ultraviolet rays.

Wels⁷⁵ found the bluish fluorescence of serum euglobulin under ultraviolet irradiation to be increased after irradiation with unfiltered ultraviolet rays.

Spiegel-Adolf⁷⁶ found also that after removing ultraviolet-coagulated serum globulin from a dilute solution, the filtrate contained a substance, probably proteose in nature, which coagulates a sol of colloidal gold. When a concentrated solution of this substance is added to spinal fluid, the mixture simulates the fluid of cases of general paralysis in the diagnostic colloidal gold precipitation test. She also showed that, after irradiation, gelatin solutions lose their protective power for gold sols and tend instead to precipitate them.⁷⁷ Arginine, histidine, lysin and choline flocculate colloidal gold only after irradiation, whereas glycine and the cyclic amino-acids do not acquire this property even after irradiation. The ability of histamine solutions (0.00018 mg. per cc.) to precipitate gold sol is lost on irradiation, although not at the same rate at which the pharmacological properties of this compound are lost. Irradiation also destroys the protective power of thymonucleic acid which becomes, like cytosine and uracil, a gold sol precipitant. Exposures up to six hours are required, however.

It has been claimed that differences between globulins and albumins exposed to ultraviolet light for varying periods, 45 minutes, 3 hours and 6 hours, can be demonstrated by the biological reaction of Abderhalden.⁷⁸ The enzymes produced by an animal in the Abderhalden reaction after the injection of such products are claimed to be specific for the kind of protein and its exposure time. It also is claimed that irradiation increases the susceptibility of globulin but not of albumin to the action of gastric juice.

⁷² A summary is given in *Arch. Path.*, **12**, 533 (1931).

⁷³ Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **190**, 28 (1927); *Klin. Wochschr.*, **7**, 1592 (1928); *Biochem. Z.*, **197**, 197 (1928).

⁷⁴ Spiegel-Adolf, M., and Oshima, Z., *Biochem. Z.*, **208**, 32 (1929); compare Spiegel-Adolf, M., and Krumpel, O., *Ibid.*, **45**, for the effects of heat on absorption.

⁷⁵ Wels, P., *Arch. ges. Physiol. (Pflüger's)*, **219**, 738 (1928).

⁷⁶ Spiegel-Adolf, M., *Biochem. J.*, **28**, 372 (1934).

⁷⁷ Spiegel-Adolf, M., *Biochem. J.*, **28**, 1201 (1934).

⁷⁸ Abderhalden, E., and Bnadze, S., *Fermentforschung*, **14**, 295 (1934); *Chem. Abs.*, **28**, 6739 (1934).

Early work of Harris⁷⁹ indicated that oxygen is absorbed during the irradiation of egg albumin, casein and edestin, but not of gelatin. At the same time, the characteristic absorption maximum at 2800Å disappears, at least in the case of egg albumin, according to Becker and Szendrő.⁸⁰ Hematoporphyrin and chlorophyll greatly accelerate the velocity of oxidation of plasma in light. This is true also, but to a lesser degree, of a number of dyes, such as methylene blue and eosin, and of ionic iron.⁸¹

Wels demonstrated⁸² that the irradiation of egg albumin in an atmosphere of nitrogen leads to the production of a substance which can be readily oxidized by oxygen or by methylene blue. This converts the substance into an oxidant capable of oxidizing the yellow leucobase of the red dye, Rosindulin GG. Irradiation under decreased oxygen tension instead of under nitrogen decreases but does not entirely prevent the formation of the substance which reduces methylene blue. After irradiation in oxygen at higher tensions, the substance is produced only in the oxidant form, capable of oxidizing the leuco-rosindulin but not of reducing methylene blue. Wels concluded from these observations that irradiated skin is the source of a substance analogous to the sulfhydryl compounds and which may play a part in tissue respiration. The property of bleaching methylene blue not shown by protein irradiated in an oxygen stream may be acquired by keeping the solution for a few hours in contact with washed frog muscle or its dry powder. The dry muscle powder bleaches methylene blue very slowly; if it is irradiated in nitrogen,⁸³ and oxidized protein is added, the bleaching is accelerated four times. Non-irradiated protein does not act.

That the reduction-oxidation potential of solutions of egg and serum albumins is reduced by coagulation either by heat or ultraviolet light has also been observed by Nakamura.⁸⁴ Kather⁸⁵ states that ultraviolet-irradiated egg albumin forms a copper-complex which is five to ten times as active as that from the non-irradiated protein in catalyzing the oxidation of unsaturated acids.

Fibrinogen is precipitated from its solutions by irradiations. Such irradiated solutions are no longer coagulated by the toxin of *Crotalus terrificus*.⁸⁶ The action of the ultraviolet light on this globulin is inhibited by the presence of hematoporphyrin.⁸⁷

Dried hide powder, after several weeks of irradiation by a quartz mercury arc, either in air or in a quartz tube under nitrogen, acquires a bright canary yellow color. Of the irradiated powder, 27.8 per cent dissolves in an equal weight of water at room temperature. The capacity of hide powder to combine with hemlock tannin at pH 3.8 is greatly reduced by the irradiation.⁸⁸

Keratin, as in unbleached horn, after ultraviolet irradiation, assumes in a lead nitrate solution a deeper color than that given by the non-irradiated sample. Wool shows a similar behavior. Thus only after irradiation do bleached horn and bleached wool acquire the ability to form lead sulfide with solutions of lead salts.⁸⁹

⁷⁹ Harris, D. T., *Biochem. J.*, **20**, 288 (1926).

⁸⁰ Becker, J. P., and Szendrő, P., *Arch. ges. Physiol. (Pflüger's)*, **228**, 755 (1931).

⁸¹ Harris, D. T., *Biochem. J.*, **20**, 280 (1926).

⁸² Wels, P., *Arch. exp. Path. Pharmacol.*, **171**, 480 (1933); *Chem. Abs.*, **27**, 5344 (1933).

⁸³ Wels, P., and Hesse, R., *Naturwiss.*, **22**, 648 (1934).

⁸⁴ Nakamura, Y., *J. Agr. Chem. Soc. Japan*, **11**, 1101 (1935); *Brit. Chem. Abs.*, **A**, 360 (1936).

⁸⁵ Kather, E., *Arch. exp. Path. Pharmacol.*, **184**, 645 (1937); *Brit. Chem. Abs.*, **A** (III), 253 (1937).

⁸⁶ Arthus, M., and Boshell, G., *Arch. intern. physiol.*, **30**, 244 (1928); *Brit. Chem. Abs.*, **A**, 1024 (1929).

⁸⁷ Howell, W. H., *Arch. intern. physiol.*, **18**, 269 (1921); *Chem. Abs.*, **16**, 935 (1922).

⁸⁸ Thomas, A. W., and Foster, S. B., *J. Am. Leather Chem. Assoc.*, **20**, 490 (1925).

⁸⁹ Beutel, E., and Kutzelnigg, A., *Monatsh.*, **64**, 183 (1934).

It is assumed that a part of the sulfur of keratin is converted into sulfur ions under the influence of light. On the other hand, Barritt and King⁹⁰ state that on exposure to ultraviolet radiations wool loses part of its sulfur as sulfur dioxide, which may be evolved, adsorbed or oxidized to sulfuric acid. From x-ray observations, Astbury and Woods⁹¹ state that irradiation of unstretched keratin by ultraviolet light or x-rays causes intramolecular changes analogous to those due to the action of water on stretched keratin.

It has been claimed that when gelatin is irradiated, it is altered in such a way as to lessen its tendency to swell in water. The effect is said to be proportional to the duration of illumination.⁹² The solubility of the swollen gelatin in water is reduced, and the irradiated solution has the property of reducing ammoniacal silver nitrate solution, but the elementary analysis is unaffected. The presence of oxygen during the irradiation is not essential. The effects of irradiation may be lessened by careful purification of the gelatin, and it has been suggested that an iron sensitizer found in the ash may be necessary for the process. Sheppard and Houck⁹³ believe the underlying reaction to be of termolecular order. According to Ponthus⁹⁴ irradiation increases the electrical conductivity and decreases the optical density and viscosity of gelatin, but does not change its state of aggregation. Duce⁹⁵ finds the surface tension to be lowered and attributes this effect to a decrease in the hydration of the colloidal particles.

Insulin is not resistant to ultraviolet rays in the presence of oxygen and it cannot, therefore, be sterilized by them.⁹⁶ Variations observed in the effect of these radiations on commercial insulin preparations have been attributed to variations in their content of phenol, which protects the preparation against their action.⁹⁷ According to Ellis and Newton,⁹⁸ exposure of commercial insulin in nitrogen in a quartz tube for 19 to 48 hours destroys the active hypoglucemic substance. Substances remain which, when injected, have the property of increasing the blood sugar level. Ozone and oxygen in sunlight destroyed the hypoglucemic substance in insulin solutions but did not develop the substances producing the increase in blood sugar in one hour.⁹⁹

Freudenberg and Wegmann¹⁰⁰ find that the activity of irradiated insulin can be partly restored by oxidation by hydrogen peroxide in the presence of cysteine. Irradiated egg-white inactivates insulin in an atmosphere of nitrogen. The photochemically liberated sulphydryl groups reduce the active disulfide form of insulin to the inactive sulphydryl form.¹⁰¹ The reducing properties may be developed in protein even by therapeutic doses of irradiation.¹⁰²

In the presence of quinones as sensitizers, hemoglobin (and also chlorophyll)

⁹⁰ Barritt, J., and King, A. T., *J. Textile Inst.*, 20, 151T, 159 (1929); *Brit. Chem. Abs.*, B, 846 (1929).

⁹¹ Astbury, W. T., and Woods, H. J., *Phil. Trans.*, 32, 333 (1933).

⁹² Brintzinger, H., and Maurer, K., *Kolloid.-Z.*, 41, 46 (1927).

⁹³ Sheppard, S. E., and Houck, R. C., *J. Phys. Chem.*, 36, 2885 (1932).

⁹⁴ Ponthus, P., *Compt. rend.*, 196, 1248 (1933).

⁹⁵ Duce, W., *Arch. ital. biol.*, 94, 34 (1935); *Boll. soc. ital. biol. sper.*, 10, 978 (1935); *Chem. Abs.*, 30, 2454 (1936); Kronenberger, F., *Boll. soc. ital. biol.*, 9, 1336 (1934).

⁹⁶ Cazzini, U., *Biochem. therap. sper.*, 16, 563 (1929); *Chem. Abs.*, 24, 917 (1930); Den Hoed, D., De Jongh, S. E., and Peck, A., *Biochem. Z.*, 205, 144 (1929).

⁹⁷ Küstner, H., and Eissner, W., *Klin. Wochschr.*, 11, 1668 (1932); *Chem. Abs.*, 27, 779 (1933).

⁹⁸ Ellis, M. M., and Newton, E. B., *Am. J. Physiol.*, 73, 530 (1925).

⁹⁹ Keeser, E., [*Arch. exp. Path. Pharmacol.*, 166, 624 (1932); *Chem. Abs.*, 26, 5582 (1932)] believes irradiation with green or blue light to activate insulin, although red light partially destroys its activity.

¹⁰⁰ Freudenberg, K., and Wegmann, T., *Z. physiol. Chem.*, 233, 159 (1935).

¹⁰¹ Kather, E., *Arch. exp. Path. Pharmacol.*, 185, 323 (1937); *Chem. Abs.*, 32, 6267 (1938).

¹⁰² Kämmerling, I., *Arch. exp. Path. Pharmacol.*, 186, 434 (1937); *Chem. Abs.*, 32, 8448 (1938).

absorb hydrogen under the influence of light.¹⁰³ Oxidation occurs subsequently, turning the quinones (with the exception of juglone), brown. In sunlight, hemoglobin is degraded into its decomposition products, the process being accelerated by the use of glutathione as sensitizer. Under these conditions, chlorophyll may be destroyed.¹⁰⁴ Lennox¹⁰⁵ states that in ultraviolet light, potassium iodide, but not free iodine, accelerates the conversion of hemoglobin to methemoglobin. Etioporphyrin I, when irradiated in pyridine containing sodium ethylate, alters its spectrum, a new absorption band appearing at 6360A, the red solution becoming blue and then green.¹⁰⁶ Oxygen is necessary for the change to occur. The solution contains etioglucobilin and a red diketone of this substance, besides a mixture of dinuclear aldehydes, very similar to etioneoxanthomethenes. The first step in the photochemical oxidation is the addition of oxygen at several of the methine bridges of the porphyrin. The resulting peroxide isomerizes and the bridge breaks to yield an isomer of glucobilin, which rearranges. The other products result from other rearrangements of the peroxide.

ENZYMES

Since the activity of an enzyme depends, in general, upon the integrity of its colloidal protein component, the destruction of the activity of enzymes is intimately bound up with the effects of ultraviolet upon the proteins. Since, however, there may conceivably be various prosthetic groups in the enzyme molecule which also condition its activity, the details of the destruction process may be expected to vary from enzyme to enzyme. Therefore, although most enzymes which have been tested have been found to be sensitive to ultraviolet rays, the behavior of each must be discussed separately. In many cases the activity of enzymes depends also upon the presence of specific coenzymes, and these also may be affected by radiations.¹⁰⁷

It has been claimed that certain monochromatic radiations in the visible range increase the activity of catalase, pepsin, trypsin, and lipase. In no case was the enzyme activity depressed.¹⁰⁸

Application of ultraviolet rays may aid in determining the unitary or non-unitary nature of certain enzymes which have the property of acting upon more than one substrate. If the activity toward each is destroyed at the same rate on irradiation of the preparation it may be assumed that but one enzyme is involved, according to Helferich and Brieger.¹⁰⁹ In the emulsion of almonds, the activity toward phenol β -D-glucoside and phenol-D-galactoside diminish at the same rate, suggesting that both substrates are hydrolyzed by the same enzyme. The activity toward phenol β -D-glucoside, however, diminished twice as rapidly as that toward phenol α -D-mannoside, suggesting that different enzymes affect these substrates.¹¹⁰

Diastase. The behavior of this enzyme has been extensively studied by Pincussen. It is not destroyed by sunlight, but is inactivated by shorter ultraviolet

¹⁰³ See also Gouzon, B., *Ann. physiol. physicochim. biol.*, **11**, 388 (1935).

¹⁰⁴ Kögel, G., *Strahlentherapie*, **42**, 379 (1931); *Brit. Chem. Abs.*, **A**, 634 (1932).

¹⁰⁵ Lennox, F. G., *Australian J. Exptl. Biol. Med. Sci.*, **13**, 193 (1935); *Brit. Chem. Abs.*, **A**, 92 (1936).

¹⁰⁶ Fischer, H., and Herrle, K., *Z. physiol. Chem.*, **251**, 85 (1938).

¹⁰⁷ An early attempt to classify enzymes in accordance with their sensitivity to ultraviolet under various conditions was made by Agulhon, H., *Compt. rend.*, **153**, 979 (1911).

¹⁰⁸ Keeser, E., *Arch. exp. Path. Pharmacol.*, **164**, 626 (1932); *Chem. Abs.*, **26**, 3269 (1932); note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

¹⁰⁹ Helferich, B., and Brieger, G., *Z. physiol. Chem.*, **221**, 94 (1933); Helferich, B., Rohr, H., and Günther, E., *Ibid.*, 90.

¹¹⁰ Note also Hill, K., *Ber. für Handlung. Sachs. Akad. Wiss. Leipzig, Math. Phys. Klasse*, **86**, 115 (1934); *Chem. Abs.*, **28**, 5843 (1934).

rays. The destruction is greatest at pH 4.6 at which the enzyme also exhibits its maximum activity. The destruction is least at pH 7.0 and 7.4.¹¹¹ The rate is accelerated by the presence of iodides and inhibited by glycine and by starch, but is but little affected by sugars or by change of temperature. In the presence of dextrose, sunlight may have a slight effect. The inactivation of 0.1-per cent malt diastase acting on 1-per cent starch solution at varying pH values proceeds as a unimolecular reaction, although in the presence of 0.5 per cent of starch only the later stages of the reaction are expressed by the unimolecular rate equation. The disagreement is still more marked in the presence of 0.25 per cent of starch. A 0.2-per cent solution of the enzyme gives complex results in the presence of either 1-, 0.5- or 0.25-per cent starch solutions.¹¹²

Phosphate solutions (6*M*) protect malt diastase and the maltase of pancreatin from inactivation by ultraviolet rays, but less dilute solutions are less effective. Similar results are given by acetate solutions of the same pH. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at pH 6.64.¹¹³ Ammonium, potassium and lithium chlorides, potassium bromide and sodium fluoride protect Taka-diastase to varying degrees, the effects being more marked in dilute solutions of these salts than in more concentrated ones. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures.

Lüers and Lorinser¹¹⁴ found the inactivation of malt amylase by ultraviolet rays followed neither the mono- nor bi-molecular reaction equations or the Schutz law. The temperature coefficient is 1.30 between 20 and 30°C.

Pincussen¹¹⁵ believed also that in alkaline solutions, irradiation increases the action of salivary and Taka-diastases, pancreatic diastases showing a similar but very much less marked response.

During the progressive purification of diastase from the pancreas, the sensitivity toward ultraviolet rays progressively increases.¹¹⁶ Diastase which had been rendered almost inactive by irradiation could be partly reactivated by the addition of small quantities of non-irradiated diastase. Since this effect is not obtained in the case of heat inactivation, the mechanisms of the two modes of inactivation were thought different.¹¹⁷

Although Kawakami¹¹⁸ was unable to confirm the inactivation of Taka-diastase by ultraviolet rays, Thompson and Hussey¹¹⁹ found the inactivation of amylase to follow a unimolecular course for 88 per cent of the process. Similar results were recorded for Taka-diastase in 0.1-per cent solution by Yamashiki.¹²⁰ The influence of the voltage at which the mercury arc was operated upon the value of the monomolecular rate constant was determined by Thompson and Tennant¹²¹ for pancreatin solutions. With 4 amperes and a potential of 75 volts, 0.02-per cent pancreatin solution at pH 6.7 gave a constant of 0.259. With 70 volts across the

¹¹¹ Pincussen, L., *Biochem. Z.*, **134**, 459 (1923); *J. Soc. Chem. Ind.*, **42A**, 370 (1923).

¹¹² Pincussen, L., and DiRenzo, F., *Biochem. Z.*, **144**, 366 (1924).

¹¹³ Pincussen, L., *Biochem. Z.*, **144**, 372 (1924); see also Terroine, E. F., and Bonnet, R., *Bull. soc. chim. biol.*, **9**, 982 (1927); *Chem. Abs.*, **22**, 1169 (1928).

¹¹⁴ Lüers, H., and Lorinser, P., *Biochem. Z.*, **144**, 212 (1924).

¹¹⁵ Pincussen, L., *Biochem. Z.*, **152**, 406 (1924).

¹¹⁶ Pincussen, L., *Fermentforschung*, **8**, 181 (1925); *Biochem. Z.*, **171**, 1 (1926). Note also Kamabayashi, Y., *Biochem. Z.*, **203**, 334 (1928).

¹¹⁷ Pincussen, L., and Oya, T., *Biochem. Z.*, **207**, 410 (1927).

¹¹⁸ Kawakami, T., *J. Pharm. Soc. Japan*, **49**, 361 (1929); *Chem. Abs.*, **23**, 4238 (1928).

¹¹⁹ Thompson, W. R., and Hussey, R., *J. Gen. Physiol.*, **15**, 9 (1931).

¹²⁰ Yamashiki, H., *Acta Schol. Med. Univ. Imp. Kyoto*, **16**, 365 (1934); *Chem. Abs.*, **28**, 4759 (1934).

¹²¹ Thompson, W. R., and Tennant, R., *J. Gen. Physiol.*, **18**, 675 (1935).

lamp it was reduced to 0.172 and with 80 volts it was raised to 0.302. The protective action of added dog serum on the stability of the solutions could be accounted for by internal filtering without the necessity of assuming for the serum a specific negative catalytic action.

Sensitizers like eosin, sodium anthraquinone disulfonate and sodium dichloroanthracene disulfonate aid various photochemical processes but have only a depressing effect upon the inactivation of Taka-diestase by ultraviolet light. Potassium ions increase the effects of light and decrease the rate of heat inactivation; the reverse is true of the calcium ion.¹²²

Diastase also may be protected from the action of ultraviolet light by the presence of asparagine, anilinoacetic acid, ammonium citrate, gelatin or tyrosine, probably by internal filtering.¹²³

Hutchinson and Ashton¹²⁴ found that full ultraviolet irradiation retards the ability of both salivary and malt diastases to produce dextrin and sugars from starch in an inverse relation to the intensity of the light used. They report also that green light had a somewhat similar effect on salivary diastase, but that both salivary and malt preparations were stimulated in their activity by either red-yellow or near ultraviolet light. Apparent differences of the rates of production of dextrans and of maltose by malt diastase during irradiation with various monochromatic radiations led them to suspect the presence of different enzymes in the preparation.

Tang and Sung¹²⁵ find fully germinated malt unaffected by ultraviolet rays, although malt which had just begun to germinate lost its activity on irradiation.

Sucrase. Preparations of this enzyme exhibit an absorption band with its maximum at about 2700A, attributed to the presence of tryptophane in the protein of the enzyme. Addition of this amino- acid protects¹²⁶ the enzyme from inactivation by ultraviolet light. Yeast gums also present in the preparations have but very little absorption at 2700A.

Although yeast autolyzates are almost uninjured by irradiation for two hours, sucrase preparations of a high degree of purity were inactivated within twenty to thirty minutes.¹²⁷ The pH had but slight effect on the course of inactivation. The curve was linear during the earlier part of the reaction, but fell off later. In the presence of molecular oxygen, there was an apparent activation during the first ten minutes of irradiation, this being ascribed to oxidation of inhibiting substances assumed to be present in the preparations employed. No reactivation could be obtained by the addition of tryptophane or yeast gums. On the contrary, these additions, particularly the yeast gums, hasten the postinactivation which occurs on standing in preparations which have been previously irradiated for ten minutes.¹²⁸

Recently, the activating effects of very brief irradiation (3650 and 3660A), of 5 minutes for autolyzates or half that long for dialyzates, was again noted by Gorbach with Ruess.¹²⁹ The effect is observed after the irradiated solutions have stood a short while, increasing to a maximum and then declining with time. Repeated short irradiations give greater activation than a single longer one.

¹²² Kumanomidoh, S., with Pincussen, L., *Biochem. Z.*, **195**, 79 (1928).

¹²³ Banerjee, S., and Sen, H. K., *J. Indian Chem. Soc.*, **12**, 379 (1935); *Chem. Abs.*, **30**, 113 (1936).

¹²⁴ Hutchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **9**, 49 (1933); *Chem. Abs.*, **27**, 5353 (1933).

¹²⁵ Tang, T.-H., and Sung, T.-T., *J. Chinese Chem. Soc.*, **5**, 174 (1937); *Chem. Abs.*, **31**, 6405 (1937).

¹²⁶ Gorbach, G., and Lerch, K., *Biochem. Z.*, **219**, 122 (1930); *Chem. Abs.*, **24**, 2769 (1930); *Biochem. Z.*, **235**, 259 (1931); *Chem. Abs.*, **25**, 4565 (1931).

¹²⁷ Gorbach, G., and Pick, H., *Monatsh.*, **61**, 29 (1932); *Chem. Abs.*, **27**, 110 (1933).

¹²⁸ Gorbach, G., and Kimovec, D., *Monatsh.*, **61**, 39 (1932); *Chem. Abs.*, **27**, 110 (1933).

¹²⁹ Gorbach, G., with Ruess, H., *Biochem. Z.*, **271**, 338 (1934); *Chem. Abs.*, **29**, 2186 (1935); *Biochem. Z.*, **280**, 213 (1935); *Chem. Abs.*, **30**, 120 (1936).

Albers and Meyer¹⁸⁰ doubt the evidence of Gorbach that tryptophane is the carrier of the enzyme activity, since, although tryptophane could be detected in the purest preparations of this enzyme, its content was not proportional to the enzyme activity. The observed increase in the absorption, particularly of the longer wave-lengths, was attributed to an aggregation of the colloidal carrier accompanied by an alteration or masking of the active groups.^{180a}

Ultraviolet light retards the action of phosphatase from tuberculous lymph glands of rabbits on calcium fructose mono- and sucrose-phosphate, but not on calcium α -glycerophosphate. In the presence of eosin, sunlight also diminished the activity of the phosphatase.¹⁸¹ Collier and Wasteneys¹⁸² find that plasma phosphatase may be destroyed by ultraviolet and by visible light.

Lipase. There have been recent claims that monochromatic radiations of long wave-length stimulate the activity of lipase. This effect, at least that on the action of the lipase of autolyzed yeast on castor oil, is said to be decreased when light of greater intensities is used.¹⁸³ Ultraviolet rays, however, inactivate lipase.¹⁸⁴ Similar observations have been recorded on the destruction of lipase in the blood serum of rabbits or guinea pigs. The proteins in the serum exert a protective action and the effects are greater when part of the protein content is removed.¹⁸⁵

Irradiation of dry powdered seeds of *Ricinus communis* does not affect their lipase activity.¹⁸⁶

Proteinases. That pepsin solutions can be inactivated by ultraviolet rays by a monomolecular reaction was observed by Hussey and Thompson and later confirmed by Gates.¹⁸⁷ Northrop¹⁸⁸ found the loss of activity of his crystalline preparations caused by either ultraviolet rays or radium to be exactly proportional to the rate of loss of proteins by denaturation. This was evidence supporting the view that the enzyme is a crystalline protein and not merely some simpler substance carried by the protein, or at any rate that the protein molecule is itself responsible for the enzyme activity of the preparation. The rate of inactivation varied with the pH of the solution; it had its maximum value at pH 2. Uehara places it at pH 1.4.¹⁸⁹

The preparations exhibit an absorption band between 2600 and 2900A. At low temperatures this may be resolved into a number of sharp narrow bands.¹⁴⁰ Gates found in a series of experiments with monochromatic ultraviolet light that the destruction of pepsin by different wave-lengths agrees in general with its absorption spectrum. Thus, by plotting the reciprocals of the energies required for various wave-lengths to produce the same degree of inactivation there is obtained a curve,

¹⁸⁰ Albers, H., and Meyer, I., *Z. physiol. Chem.*, **228**, 122 (1934).

^{180a} This, however, may be not necessarily the case since similar increases in absorption during brief irradiation periods have been observed in crystalline pepsin and uracil solutions where there is no possibility of the presence of a carrier of high molecular weight.

¹⁸¹ Horii, I., *Arb. Inst. Univ. Kyoto*, III C, 62, 1931; *Brit. Chem. Abs.*, A, 874 (1932).

¹⁸² Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

¹⁸³ Murakami, R., *J. Agr. Chem. Soc. Japan*, **12**, 709 (1936); *Chem. Abs.*, **31**, 1436 (1937). This author made similar observations on yeast amylase, proteinase and urease, *J. Agr. Chem. Soc. Japan*, **12**, 175, 180 (1936); **12**, 151; **13**, 46 (1937).

¹⁸⁴ Takayama, T., *Bull. Agr. Chem. Soc. Japan*, **5**, 71 (1929); *Chem. Abs.*, **25**, 123 (1931).

¹⁸⁵ Pincussen, L., and Hayashi, S., *Biochem. Z.*, **195**, 196 (1928).

¹⁸⁶ Cousin, E., and Creach, P., *Bull. soc. pharm. Bordeaux*, **75**, 12 (1937); *Chem. Abs.*, **31**, 6681 (1937).

¹⁸⁷ Gates, F. L., *J. Gen. Physiol.*, **17**, 797 (1933-4); **18**, 265 (1934).

¹⁸⁸ Northrop, J. H., *J. Gen. Physiol.*, **17**, 359 (1934).

¹⁸⁹ Pincussen, L., and Uehara, K., *Biochem. Z.*, **195**, 87 (1928).

¹⁴⁰ Lavin, G. I., Northrop, J. H., and Taylor, H. S., *J. Am. Chem. Soc.*, **55**, 3497 (1933); **57**, 874 (1935).

the destruction spectrum, which is similar in form and location to the absorption spectrum. During the process of irradiation, an increase in absorption occurs at wave-lengths other than that of the maximum absorption. Thus the minimum in the absorption spectrum at about 2500Å was gradually lost and the long wave-length leg of the absorption curve also showed a very considerable increase in absorption.¹⁴¹ A protective action by proteins also has been observed in the case of this enzyme by Banerjee and Sen.¹⁴²

Trypsin also is inactivated by ultraviolet but not by visible rays. The effect is maximal in the absence of iodides of the alkalis or alkaline earths.¹⁴³

The eosin-sensitized photochemical destruction of rennet by visible light follows a unimolecular course, the rate constant being independent of the time of irradiation until 60 per cent of the enzyme has weakened. Its value increases with the concentration of the enzyme and is proportional to the intensity of illumination.¹⁴⁴

Purified tyrosinase can be injured by irradiation, according to Pincussen and Hammerich.¹⁴⁵ It is suggested that this may in some manner be concerned with the formation of melanins from tyrosine or related substances in irradiated skin. Alverdes¹⁴⁶ believed that yellow rays promote the activity of the tyrosinase of the larvae of *Cyclops viridis*.

The destruction and absorption spectra of urease in the ultraviolet region are believed coincident by Kubowitz and Haas.¹⁴⁷ According to Pincussen and Kato,¹⁴⁸ sunlight acting on urease solutions at pH 6.4 diminished the activity both of the active constituents and of a so-called "stable Component-X." Potassium hydrogen phosphate at pH 5.6 affords partial protection to the active component, but even in darkness the activity of the other constituents is decreased by phosphate. Ultraviolet irradiation destroys the active enzyme both in the presence and absence of phosphate, but does not have such a marked effect as sunlight in inhibiting Component X. Collier and Wasteneys¹⁴⁹ found that impure urease may be destroyed not only by ultraviolet but also by infrared rays. The quantity of ammonia produced by soy urease is said, however, to increase with the intensity of monochromatic light of various wave-lengths tested by Murakami.¹⁵⁰ Crystalline urease is rapidly destroyed by ultraviolet irradiation and cannot be reactivated by reducing agents or tissue extracts. Irradiated urease produces no antiurease when injected into animals.¹⁵¹

Ultraviolet rays decrease the activity of animal rennet, although they have no effect on the rennet derived from plants, such as thistle blossoms.¹⁵² Ultraviolet light destroys thrombin, but prothrombin is more resistant, according to Cekada.¹⁵³

¹⁴¹ Note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

¹⁴² Banerjee, S., and Sen, H. K., *J. Indian Chem. Soc.*, **12**, 740 (1935); *Chem. Abs.*, **30**, 2581 (1936).

¹⁴³ Pincussen, L., and Klissianis, N., *Biochem. Z.*, **152**, 416 (1924); Pace, J., *Ibid.*, **240**, 490 (1931).

¹⁴⁴ Schmidt-Nielsen, S., and Fjermeros, E., *Compt. rend trav. lab. Carlsberg, Sér. chim.*, **22**, 473 (1938); *Chem. Abs.*, **32**, 6266 (1938).

¹⁴⁵ Pincussen, L., and Hammerich, T., *Biochem. Z.*, **239**, 273 (1931).

¹⁴⁶ Alverdes, E., *Archiv Entwickl. Organ.*, **47**, 375 (1921).

¹⁴⁷ Kubowitz, F., and Haas, E., *Biochem. Z.*, **257**, 337 (1933).

¹⁴⁸ Pincussen, L., and Kato, N., *Biochem. Z.*, **142**, 228 (1923).

¹⁴⁹ Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

¹⁵⁰ Murakami, R. J., *Agr. Chem. Soc. Japan*, **13**, 439 (1937); *Chem. Abs.*, **32**, 1723 (1938).

¹⁵¹ Pillemer, L., Ecker, E. E., Myers, V. C., and Muntwyler, E., *J. Biol. Chem.*, **123**, 365 (1938).

¹⁵² Christen, C., and Virasoro, E., *Lait*, **15**, 354, 496 (1935); *Chem. Abs.*, **29**, 5134 (1935).

¹⁵³ Cekada, E. B., *Am. J. Physiol.*, **78**, 512 (1926). For the behavior of baicalinase, see Miwa, T., *Acta Physicochim.*, **9**, 89 (1936); *Chem. Abs.*, **30**, 8272 (1936), and for β -glucuronosidase, Oshima, G., *J. Biochem. (Japan)*, **23**, 305 (1936); *Chem. Abs.*, **30**, 4882 (1936).

Enzymes Concerned with Respiration. Ito¹⁵⁴ noted that catalase has two absorption bands at 4060 and 2660A, the first corresponding to the absorption band of hemin. Quite different was the earlier statement by Kuhn, Hand and Florkin¹⁵⁵ that the absorption spectrum of catalase shows three bands at 6290, 5400 and 5000A, in contrast to the continuous visible absorption of peroxidase. Zeile and Hellström¹⁵⁶ also gave absorption spectral evidence that liver catalase contained a porphyrin iron complex, the carrier of the catalase function.

Blood catalase is more readily destroyed in dilute than in stronger solutions, and the most rapidly at pH 6.81, the optimum for its activity.¹⁵⁷ The addition of salts protected the catalase from the action of light. In the case of potassium iodide, the results were complicated by the action of the iodine liberated by the light. Morgulis and Schumacher¹⁵⁸ found that the process proceeds at a uniform rate at pH 6.28. At more acid or alkaline reactions, the initial rate of inactivation diminishes considerably with the lapse of time. At pH 11, this effect is so marked that the enzyme may be said to be actually stabilized against the radiations.

Spectrographic determinations have been used in an original manner by Stern¹⁵⁹ in following the formation of intermediate compounds during the action of this enzyme. He noted that purified catalase solutions show, in addition to the hematin absorption in the visible regions, ultraviolet bands due to the protein carrier. These varied with the source from which the catalase had been prepared. Irradiation from a mercury lamp inactivated the enzyme and changed its fluorescence from yellow-green to blue-green. This effect did not occur if a nickel oxide filter was interposed.

Califano¹⁶⁰ believed that by irradiation with blue mercury lines 4050 to 4360A, the intensity of catalase activity is decreased. There is little action by 4920A and none by 5460 and 5780A. The compound of catalase and carbon monoxide is decomposed by the 4050A line and less so by that at 4920A.

Ultraviolet irradiation of yeast cells has been claimed to increase their catalase activity several times.¹⁶¹ After 16 to 18 hours it increases 300 per cent in *Saccharomyces ellipsoideus*, 1000 per cent in *Torula rosa* and 2500 per cent in *Torula colliculosa*. However, there was only a slight increase in the case of silkworm eggs.¹⁶²

Green-colored rice may be decolorized by sunlight, but not by ultraviolet rays. During this process, the catalase and peroxidase activities decreased remarkably, but this also did not occur when ultraviolet rays were used.¹⁶³

From absorption data, Kuhn, Hand and Florkin¹⁶⁴ believed it probable that the active group in peroxidase is an iron porphyrin compound. The absorption

¹⁵⁴ Ito, R., *J. Biochem., Japan*, **22**, 139 (1935); *Chem. Abs.*, **29**, 8025 (1935).

¹⁵⁵ Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.*, **201**, 255 (1931).

¹⁵⁶ Zeile, K., and Hellström, H., *Z. physiol. Chem.*, **192**, 171 (1930). See also Stern, K. G., *J. Biol. Chem.*, **121**, 561 (1937).

¹⁵⁷ Pincussen, L., and Seligsohn, F., *Biochem. Z.*, **168**, 457 (1926).

¹⁵⁸ Morgulis, S., and Schumacher, L., *J. Biochem.*, **86**, 75 (1930).

¹⁵⁹ Stern, K. G., *Nature*, **136**, 335 (1935); **136**, 302 (1935); *Z. physiol. Chem.*, **212**, 207 (1932); **219**, 105 (1933).

¹⁶⁰ Califano, L., *Naturwiss.*, **22**, 249 (1934); *Chem. Abs.*, **28**, 5478 (1934).

¹⁶¹ van Euler, H., and Günther, G., *Z. physiol. Chem.*, **220**, 69 (1933); *Chem. Abs.*, **27**, 5343 (1933). Variations in intensity are believed more significant than variations in wave-length by Murakami, R., *J. Agr. Chem. Soc. Japan*, **13**, 429, 435 (1937); *Chem. Abs.*, **32**, 1723 (1938).

¹⁶² Yamafuji, K., *Enzymologia*, **1**, 120 (1936); **2**, 147 (1937); *Chem. Abs.*, **30**, 7600 (1936); **32**, 9101 (1938). Similar observations on *Spinogrya* were recorded by Burge, W. E., and Burge, E. L., *Bot. Gaz.*, **77**, 220 (1924).

¹⁶³ Kondo, M., and Okamura, T., *J. Sci. Agr. Soc. Japan*, No 327, 67 (1931); *Chem. Abs.*, **25**, 5689 (1931).

¹⁶⁴ Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.*, **201**, 255 (1931).

appeared to be continuous and located in the visible region. Peroxidase inhibited by carbon monoxide could not be reactivated by light. According to Pincussen and Hammerich¹⁶⁵ this enzyme is destroyed also by the rays of the quartz mercury arc, the loss of activity being almost proportional to the light intensity. Aside from the fact that the greatest destruction occurs in acid solution, the pH has relatively little influence upon the process.

An enzyme of the liver which oxidizes ethyl alcohol is also inactivated by ultraviolet light.¹⁶⁶ Keilin¹⁶⁷ believes the indophenol oxidase system of yeast cells which has been impaired by combination with carbon monoxide may be regenerated by the dissociating action of light.

The xanthine oxidase obtainable from milk may be inactivated by sunlight, ultraviolet light or radium, according to Toyama.¹⁶⁸ Its absorption band has a maximum at 2790Å; this is shifted toward greater wave-lengths in an alkaline medium.¹⁶⁹

The action of a specific dehydrogenase in decolorizing methylene blue in the presence of alcohol as the hydrogen donor in an evacuated Thunberg tube may be accelerated by irradiation with a quartz mercury lamp.¹⁷⁰ According to von Euler and Klusmann,¹⁷¹ this is not due to a rise in temperature, to a photochemical action on the dye alone, or to photooxidation of the yeast extract. The effect is absent if a succino-dehydrogenase or liver extract system is used, but the effect is observed when apozymase and cozymase are used instead of yeast. von Euler, Hellström and Brandt¹⁷² believe that the reduction of methylene blue in a dehydrase-alcohol system is accelerated by red light. A photoreduction of methylene blue likewise takes place in the absence of enzymes in the presence of alcohol as the hydrogen donor. The number of reduced dye molecules varied from one to 6000 to one to 35 quanta under various conditions with red and with ultraviolet light. At pH 5.1, the reduction is one hundred times as fast as at pH 7. The reduction is accelerated by ferrous ions. The irradiated dye fluoresces; a single band appears at 6780 to 6800Å.

The dehydrogenase of beef liver represents a complex system in which, besides glucose and the enzyme itself, there are also present a coenzyme and a flavin-enzyme. Adler and von Euler¹⁷³ found that green and blue light did not affect the reaction velocity, but a red filter (675 to 645 mμ), which corresponds to the absorption maximum of methylene blue, was effective in activating the system. This means that the photoactivation occurs upon the dye. Illumination of the complete system with visible light doubles the reaction velocity. In the absence of flavin, the reaction proceeds normally if light is supplied, so that the flavin does not participate in the light activity. Inhibition by copper occurs in light or darkness and in the presence or absence of flavin, so that it must represent a direct effect upon the dehydrogenating enzyme. That cozymase is an indispensable component of the system shows it to be functionally interdependent with dehydrogenase. When a constant light intensity is used, the speed of inactivation decreases with

¹⁶⁵ Pincussen, L., and Hammerich, T., *Biochem. Z.*, **241**, 384 (1931).

¹⁶⁶ Mizusawa, H., *J. Biochem. Japan*, **18**, 243 (1933); *Chem. Abs.*, **28**, 794 (1934).

¹⁶⁷ Keilin, D., *Nature*, **119**, 670 (1927).

¹⁶⁸ Toyama, J., *Fukwoka-Ikwadai Gaku-Zasshi*, **26**, 1483 (1933); *Chem. Abs.*, **28**, 7279 (1936).

¹⁶⁹ Ito, R., *J. Biochem. Japan*, **22**, 139 (1935); *Chem. Abs.*, **29**, 8025 (1935).

¹⁷⁰ Krestownikoff, A. N., *Skand. Arch. Physiol.*, **52**, 199 (1927); *Brit. Chem. Abs.*, **A**, 445 (1928).

¹⁷¹ von Euler, H., and Klusmann, E., *Naturwiss.*, **22**, 777 (1934); von Euler, H., *Arkiv Kemi, Mineral Geol.*, **11B**, 45 (1934).

¹⁷² von Euler, H., Hellström, H., and Brandt, K., *Naturwiss.*, **23**, 486 (1935).

¹⁷³ Adler, E., and von Euler, H., *Z. physiol. Chem.*, **232**, 6, 10, 16 (1935).

increasing cozymase concentration.¹⁷⁴ Cozymase differs from the coenzyme of the Warburg dehydrogenase in that the former but not the latter can be destroyed in solutions as concentrated as one mg. per cc.

Junghagen¹⁷⁵ finds the dehydrogenases of pyruvic and glycerophosphoric acids to be rapidly destroyed by ultraviolet light. In the range between pH 6 and 8, succinodehydrogenase is also injured by ultraviolet light, but the destruction is not so rapid in acid solutions.¹⁷⁶ Exposure to ordinary light for an hour also causes injury, but exposure for only half an hour merely stimulates the activity of the enzyme.

Warburg¹⁷⁷ made extensive use of irradiation and spectrographic methods in his investigations of his new hemin-containing respiratory enzyme.

He found its compound with carbon monoxide to be dissociable by light; and, by quantitative determinations of the intensities of various wave-lengths required to produce a given amount of destruction, determined the absorption spectrum of the carbon monoxide compound of the enzyme.¹⁷⁸ Irradiation of yeast cells with equal intensities of monochromatic light of various wave-lengths caused an increase in the rate of respiration of the cells. By plotting this effect against the wave-lengths, he obtained a curve of the absorption of light by the hemin of the enzyme. The spectrum of the respiratory enzyme so obtained is similar in shape to the absorption curve of the carbon monoxide compound of reduced hemin. The maximum of the latter curve is, however, at 408 m μ , and that of the respiratory enzyme is at 436 m μ . This discrepancy is accounted for by the assumption that the respiratory enzyme exists in the solid state adsorbed on the surface of the cells.

In the course of these investigations the absorption spectra of carbon monoxide, iron carbonyl, pyridine-hemin, and the compound of carbon monoxide and ferrocysteine were examined. These comparative absorption spectra show not merely that the iron carbonyl group is a part of the respiratory enzyme but also that it is attached to a hemin-like molecule. The absorption curve for the carbon monoxide-ferrocysteine compound is quite different.¹⁷⁹ Warburg, Negelein and Christian¹⁸⁰ found carbon monoxide-hemoglobin in carbylamine solutions to be the most light-sensitive carbon monoxide-iron-porphyrin compound then known.

In tissue sections, a blue fluorescence in Wood's light due to proteins gives way on continued irradiation to a red fluorescence characteristic of free porphyrin liberated from any complexes present by photolysis.¹⁸¹

A respiratory enzyme derived from the retina has an absorption spectrum identical with that of the enzyme derived from yeast.¹⁸² The respiratory enzyme differs from cytochrome. A new yellow oxidation enzyme is also obtainable from bottom yeast.¹⁸³ Its absorption spectrum has three bands, two of which, at 465 and 495 m μ , are in the long wave-length range.¹⁸⁴ The enzyme has an active group, a reversible yellow pigment, bound to a colloidal protein carrier. The active group can be split from the protein by aqueous methanol. It fluoresces green and is catalytically inactive, but the light absorption in the visible range is almost unchanged. It has two bands in the ultraviolet at 2700 and 3500A, and also one at 4450A.¹⁸⁵ When irradiated in dilute alkaline solution,

¹⁷⁴ von Euler, H., and Schlenk. *Arkiv Kemi, Mineral Geol.*, **12B**, No. 19 (1936).

¹⁷⁵ Junghagen, S., *Skand. Arch. Physiol.*, **54**, 115 (1928); *Chem. Abs.*, **22**, 4549 (1928).

¹⁷⁶ Pincussen, L., and Roman, W., *Biochem. Z.*, **229**, 281 (1930).

¹⁷⁷ Warburg, O., *Naturwiss.*, **16**, 345 (1928); Warburg, O., and Negelein, E., *Naturwiss.*, **16**, 856 (1928); *Biochem. Z.*, **202**, 202 (1928).

¹⁷⁸ Warburg, O., and Negelein, E., *Biochem. Z.*, **214**, 64 (1929).

¹⁷⁹ Cf. also Cremer, W., *Biochem. Z.*, **194**, 231 (1928); Krebs, H. A., *Ibid.*, **193**, 347 (1928). For the splitting by light of the carbon monoxide-ferroglutathione compound, see Kubowitz, F., *Biochem. Z.*, **282**, 277 (1934).

¹⁸⁰ Warburg, O., Negelein, E., and Christian, W., *Biochem. Z.*, **214**, 26 (1929).

¹⁸¹ Thomas, J., *Compt. rend. soc. biol.*, **125**, 386 (1937); *Chem. Abs.*, **31**, 6681 (1937).

¹⁸² Warburg, O., and Negelein, E., *Biochem. Z.*, **214**, 101 (1929).

¹⁸³ Warburg, O., and Christian, W., *Biochem. Z.*, **254**, 438 (1932).

¹⁸⁴ Warburg, O., and Christian, W., *Naturwiss.*, **20**, 980 (1932); Kubowitz, F., and Haas, E., *Biochem. Z.*, **255**, 247 (1932).

¹⁸⁵ *Biochem. Z.*, **258**, 496 (1933); **263**, 228 (1933); **266**, 377 (1933).

the active component, after acidification, becomes soluble in chloroform. It yields a crystalline derivative, $C_{13}H_{12}N_4O_2$, from which it is possible to obtain urea and a compound, $C_6H_{10}N_2O_2$.¹⁸⁶ Theorell¹⁸⁷ has recently found the yellow coenzyme portion obtained after separation from the protein to consist of a flavine esterified with phosphoric acid and therefore related to the vitamin B_2 of the German workers.^{187a}

Bénard, Biancani, and Biancani¹⁸⁸ observed that ultraviolet light dissociates the compound of carbon monoxide with hemoglobin.

Warburg and Christian¹⁸⁹ find that the irradiation of one microgram of their hydrogen-transferring coenzyme in 1 cc. of water with a quartz lamp destroys its catalytic activity in fifteen minutes. In a glass tube or with a solution a thousand times as concentrated, there is no measurable destruction in this time. The time required for the half destruction by an intensity of one calorie per square meter per minute (calculated from data obtained at other intensities) increases with the wave-length. It is 520 times as large at 2830 Å as at 1860 Å. From an analysis of the data, the conclusion is drawn that not all of the light absorbed, but only that absorbed by a special group in the coenzyme, brings about its destruction.

The work on the relation of ultraviolet light to the respiratory enzymes has been extensively reviewed by Wynd and Reynolds.¹⁹⁰

HORMONES¹⁹¹

Künster¹⁹² claims that the actions of various plant hormones are materially affected by irradiation.

The effects of ultraviolet light on insulin have been discussed in connection with the proteins. Adrenaline, according to Keeser,¹⁹³ is activated by red and green light and inhibited by blue light. Pennetti¹⁹⁴ states that, in the presence of eosin, adrenalin may be inactivated by sunlight. Some protective power is exerted against this action by pyrogallol, hydroquinone and resorcinol, but not by gelatin, egg albumin, Witte's peptone or glucose. Absorption data for adrenaline and ephedrine have been given by Marchlewski and Skarzynski,¹⁹⁵ who find that the stereoisomers of these products have identical absorption spectra.

The rate of oxidation of commercial adrenaline solutions with hydrogen peroxide and in light is independent of the pH, but in pure solutions of the hydrochloride an increase in rate with increase in pH can be observed. The intensity of the photooxidation depends on the intensity and wave-lengths of the light employed; irradiation with ultraviolet light alone is said to cause less change than when both visible and invisible rays are used.¹⁹⁶

Ephedrine solutions are unstable in sunlight, benzalephedrine being one of the

¹⁸⁶ See also Warburg, O., and Haas, E., *Naturwiss.*, 22, 20 (1934).

¹⁸⁷ Theorell, H., *Biochem. Z.*, 278, 263 (1935).

^{187a} (See Chapter 42.)

¹⁸⁸ Bénard, H., Biancani, E., and Biancani, H., *Compt. rend. soc. biol.*, 92, 1031 (1925); *Chem. Abs.*, 19, 3278 (1925).

¹⁸⁹ Warburg, O., and Christian, W., *Biochem. Z.*, 282, 221 (1935).

¹⁹⁰ Wynd, F. L., and Reynolds, E. S., *Ann. Mo. Bot. Gardens*, 22, 771 (1935).

¹⁹¹ It has been proposed to treat glands of internal secretion with ultraviolet light in order to render them or their extracts increasingly active. Eichelbaum G., and Altenburg, J., *British P.* 275,183, June 21, 1927; *Brit. Chem. Abs.*, B, 874 (1928).

¹⁹² Küstner, H., *Deut. Med. Wochschr.*, 58, 625 (1932); *Chem. Abs.*, 26, 4831 (1932).

¹⁹³ Keeser, E., *Arch. exp. Path. Pharmacol.*, 166, 624 (1932).

¹⁹⁴ Pennetti, G., *Arch. sci. biol.*, 9, 398 (1927); *Chem. Abs.*, 21, 3678 (1927).

¹⁹⁵ Marchlewski, L., and Skarzynski, B., *Bull. intern. acad. Polonaise*, A, 241 (1929); *Chem. Abs.*, 24, 873 (1930).

¹⁹⁶ Vacek, T., *Compt. rend. soc. biol.*, 109, 583 (1929); *Chem. Abs.*, 25, 1330 (1931).

¹⁹⁷ Moore, E. E., and Moore, M. B., *Ind. Eng. Chem.*, 23, 21 (1931).

chief decomposition products.¹⁹⁷ It was claimed by Terata and Ito¹⁹⁸ that adrenalin gains in potency (depression of intestinal motility, stimulation of uterus and vasoconstrictor action) after ultraviolet irradiation or after artificial light treatment. Ten "sunlight units," however, decreased its action. Verda, Kneer and Burge¹⁹⁹ find 1:15,000 solutions to lose their pressor effect after quartz lamp treatment. Haddock²⁰⁰ states that the effects are not marked and involve mainly racemization and slight oxidation. Ewing²⁰¹ finds the physiological activity of adrenalin solutions to be completely destroyed by exposure to ultraviolet light. The decomposition products, which have no pressor action, are similar to those formed by the action of hydrogen peroxide. The activity of solutions of synephrine salts and of *p*-hydroxyphenylpropanolamine is markedly increased by moderate, but destroyed by excessive, irradiation. The activity of solutions of synephrine base is not changed by irradiation.²⁰²

Prolan is inactivated by ultraviolet rays. Zondek and von Euler²⁰³ believed the thermal stability so similar to the ultraviolet stability as to support the view that prolan is a catalyst of enzymic nature. The absorption maximum for follicular hormones lies at 2800 to 2850 Å.²⁰⁴ Concentrates of the oxytocic hormone of the pituitary glands are inactivated by ultraviolet rays.²⁰⁵ The same is true of the hormones of the ovarian follicles and placenta, the destruction probably being by oxidation.²⁰⁶

The Schering-Kahlbaum Co.²⁰⁷ propose the ultraviolet irradiation of extracts of germinal gland hormones.

When human thyroid gland pulp is subjected to ultraviolet irradiation, iodine ions separate to the extent of 0.5 to 2.7 per cent of the total iodine content.²⁰⁸ Westra and Hunter²⁰⁹ exposed finely hashed non-goitrogenic cabbage in thin layers at 50 cm. from a mercury-vapor lamp for thirty to 120 minutes. Rabbits fed exclusively on this cabbage for twelve weeks did not develop goitre.

Secretin is quickly inactivated by ultraviolet irradiation. The absorption of ultraviolet light is thereby increased, probably because of the absorption of aldehydes formed by an extensive decomposition of the molecule. All the nitrogen is freed as ammonia.²¹⁰ Although secretin is destroyed, the villikin in extracts from the intestinal mucosa is not; this favors the independent nature of these substances.²¹¹

¹⁹⁸ Terata, B., and Ito, R. *Folia Pharmacol. Japon.*, 12, No. 1, 74; No. 2, 125 (1931); *Chem. Abs.*, 25, 3127, 5708 (1931); *Manshu Igaku Zasshi*, 26, 619, 863 (1937); *Chem. Abs.*, 32, 8453 (1938).

¹⁹⁹ Verda, D. J., Kneer, L., and Burge, W. E., *J. Pharmacol.*, 42, 383 (1931); *Chem. Abs.*, 25, 5935 (1931). See also Ewing, P. L., Blickensdofer, P., and McGuigan, H., *J. Pharmacol.*, 43, 125 (1931); *Chem. Abs.*, 26, 1004 (1932).

²⁰⁰ Haddock, L. A., *Quart. J. Pharm. Pharmacol.*, 6, 496 (1933); *Chem. Abs.*, 28, 1137 (1936).

²⁰¹ Ewing, P. L., *I. Lab. Clin. Med.*, 20, 16 (1934); *Chem. Abs.*, 29, 2233 (1935).

²⁰² See also Higgins, J. A., Ewing, P. L., and McGuigan, H. A., *J. Pharmacol.*, 44, 353 (1932); *Chem. Abs.*, 26, 3302 (1932).

²⁰³ Zondek, B., and von Euler, H., *Skand. Arch. Physiol.*, 68, 232 (1934); *Chem. Abs.*, 28, 4085 (1934).

²⁰⁴ Slotta, K. H., Ruschig, H., and Fels, E., *Ber.*, 67B, 1270 (1934); Fernholz, E., *Ibid.*, 1855; Butenandt, A., and Schmidt, J., *Ibid.*, 2088; von Euler, H., and Brandt, K., *Arkiv Kemi, Mineral Geol.*, 11B, 51 (1935); *Naturwiss.*, 23, 544 (1935); Chevallier, A., Cornil, L., and Verdollin, J., *Bull. Acad. Med.*, 114, 171 (1935); *Chem. Abs.*, 29, 8088 (1935). Bugyi, B., *Z. ges. exptl. Med.*, 101, 14 (1937).

²⁰⁵ Das, N., and Guha, B. C., *Indian J. Med. Research*, 21, 765 (1934); *Chem. Abs.*, 29, 1150 (1935).

²⁰⁶ Allen, E., and Ellis, M. M., *J. Am. Med. Assoc.*, 85, 94 (1925).

²⁰⁷ British P. 295,361, Aug. 8, 1927, to Schering-Kahlbaum Co.; *Brit. Chem. Abs.*, B, 37 (1930).

²⁰⁸ Lieben, F., and Kraus, H., *Biochem. Z.*, 236, 182 (1931).

²⁰⁹ Westra, J. J., and Hunter, V., *Proc. Soc. Exp. Biol. Med.*, 30, 1157 (1933); *Chem. Abs.*, 28, 814 (1934).

²¹⁰ Agren, G., *Skand. Arch. Physiol.*, 70, 10 (1934); *Chem. Abs.*, 29, 1475 (1935).

²¹¹ Ludany, G., *Biochem. Z.*, 285, 192 (1936).

Irradiation of an alkaline extract of the pigment hormone of the posterior lobe of the hypophysis does not affect its ability to cause on injection a temperature decrease and a blood sugar increase.²¹²

PRODUCTS OF PATHOLOGICAL SIGNIFICANCE

The toxin, ricin, could not be destroyed by ultraviolet light of wave-lengths 2250 to 2540A in experiments by Carmichael.²¹³

Irradiation of tetanus toxin destroys its toxic but not its antigenic powers.²¹⁴ The toxicity of diphtheria toxin is also destroyed.²¹⁵ Irradiation for 48 hours causes a marked change in the absorption curve.²¹⁶

Tuberculin. High dilutions of tuberculin are markedly inactivated by intense exposures to the quartz lamp.²¹⁷ The inactivity of light of short wave-lengths on concentrated "old tuberculin" was considered to be due to the lack of penetration of these rays. In weaker solutions, the activity on intracutaneous injection is diminished but the general reacting power is retained. The therapeutic use of light-treated tuberculin is recommended therefore as obviating the painful cutaneous reactions. This preparation is called ultratuberculin.

After irradiation, the "old tuberculin" solutions were incapable of causing intracutaneous reactions in tuberculosis guinea pigs and in suitable doses did not kill tuberculous guinea pigs.²¹⁸ This is in distinction to the results obtained in man, where rayed tuberculin produced both focal and general reactions. This difference is explained by assuming either that unchanged tuberculin is still present after irradiation or that the reactions in man are of a non-specific nature.

During irradiation of tuberculin, the pH of the solutions shifted toward the acid side and the surface tension increased, according to Mikhailovski.²¹⁹ Spiegel-Adolf and Seibert²²⁰ measured the ultraviolet absorption spectra of highly purified tuberculin preparations made from various organisms. Considerable variations in absorption were observed. All preparations made from human type bacilli by precipitation with trichloroacetic acid contained a substance showing selective absorption with a maximum at 2650 to 2670A, spectrographically identical with nucleic acid. Nevertheless, the content of nucleic acid as measured by the absorption band could not be correlated with the biological activity of the preparations, since some in which the absorption band was missing were still biologically active. When preparations in 0.1-per cent and 1-per cent concentrations were irradiated in a quartz-covered dish for six to ten hours at 15 cm. from a quartz mercury arc, the absorption band disappeared and the toxicity, as measured by the intradermal test and the lethal action on tuberculous guinea pigs, was lost. Thus, although nucleic acid does not appear to be identical with the potent principle of tuberculin, there seems nevertheless some sort of association between it and the potent principle.

²¹² Jores, A., *Z. ges. expl. Med.*, **91**, 207 (1935).

²¹³ Carmichael, E. B., *J. Pharmacol. Exp. Therap.*, **35**, 193 (1929).

²¹⁴ Megrail, E., and Welch, H., *Proc. Soc. Biol. Med.*, **28**, 494 (1931).

²¹⁵ Nakayama, Y., *Japan. J. Microbiol. Path.*, **21**, 990 (1933); *Chem. Abs.*, **27**, 4581 (1933); Lowenstein, Vienna *Z. Path. Therap.*, **15**, 279 (1914); *Chem. Abs.*, **9**, 653 (1915).

²¹⁶ Levaditi, C., Loiseau, G., Paic, M., Philippe, M., and Haber, P., *Compt. rend. soc. biol.*, **116**, 609 (1934); *Chem. Abs.*, **28**, 5846 (1934). For further absorption data, see Ottensooser, F., Krupski, A., and Almasy, F., *Biochem. Z.*, **277**, 314 (1935) and Wadsworth, A., Crowe, M. O'L., and Smith, L. A., *Brit. J. Exptl. Path.*, **16**, 201 (1935). From the absorption data, the presence of a hemochromogen is indicated.

²¹⁷ Hausmann, W., Neumann, W., and Schuberth, K., *Z. Tuberk.*, **46**, 32 (1926); *Chem. Abs.*, **21**, 3678 (1927); *Z. Tuberk.*, **47**, 113 (1927); *Chem. Abs.*, **22**, 985 (1928).

²¹⁸ Fischer, A., and Hausmann, W., *Z. Tuberk.*, **58**, 328 (1930); *Chem. Abs.*, **26**, 511 (1932).

²¹⁹ Mikhailovski, S. M., *Zhur. Exp. Biol. Med.*, **9**, 12 (1928); *Chem. Abs.*, **22**, 2760 (1928).

²²⁰ Spiegel-Adolf, M., and Seibert, F. B., *J. Biol. Chem.*, **106**, 373 (1934).

The action of cobra venom on red blood cells is completely destroyed by irradiating it in a dilution of 1 to 2000 in quartz with 72 times an erythema dose of the radiations from a mercury arc at a distance of half a meter.²²¹ At the same time the toxicity of the venom toward white mice was destroyed or greatly reduced. The possibility of using such attenuated venom in prophylactic treatments is suggested.

Arthus and Collins²²² found also that the toxins of *Crotalus terrificus*, *Lachesis lanceolatus*, *Vipera Russellii*, and *Naja tripudians* are decomposed by ultraviolet irradiation. The ability of cobra venom to inhibit coagulation was sometimes so changed as to cause a slight acceleration of coagulation. Snake venom could be protected from the effects of irradiation by egg-white, horse serum or Witte's peptone. Anticobra, antidaboia and antiothrops sera were little affected by irradiation unless diluted. Arthus²²³ later stated that in the presence of gelatin, the effect of the treatment was to destroy both the toxicity and the antigenic power of cobra venom. Macht and Davis²²⁴ also found ultraviolet rays to produce a rapid decrease in the potency of snake venom.

Serum "kallikrein" bound by gland activator is destroyed by ultraviolet light, the rate being largely independent of the pH.²²⁵

The flocculation characteristics of diphtheria toxoid are not changed after two to three hours of exposure to unfiltered mercury arc radiations, but the flocculating ability of the toxins decreased gradually. Their toxicity decreased about 30 per cent. The antisera lost their flocculating power and not more than 30 per cent of their antitoxic power, although their behavior as regards precipitation by sodium sulfate was not affected.²²⁶

²²¹ Much, Peemöller and Haim, *Münch. Med. Wochschr.*, 74, 1365; *Chem. Abs.*, 22, 4641 (1928).

²²² Arthus, M., and Collins, H., *Arch. Intern. Physiol.*, 30, 250 (1928); *Chem. Abs.*, 24, 2172 (1930); *Brit. Chem. Abs.*, A, 1024 (1929).

²²³ Arthus, M., *Compt. rend. soc. biol.*, 103, 130 (1930); *Chem. Abs.*, 25, 135 (1931).

²²⁴ Macht, D. I., and Davis, M. E., *Proc. Soc. Exptl. Biol. Med.*, 30, 990 (1933); note also Fulchignoni, E., *Boll. soc. ital. biol. sper.*, 11, 429 (1936); Kopaczewski, W., *Compt. rend. soc. biol.*, 80, 884 (1917).

²²⁵ Werle, E., *Biochem. Z.*, 287, 235 (1936); *Chem. Abs.*, 31, 149 (1931).

²²⁶ Modern, F., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires)*, 7, 618 (1936); *Chem. Abs.*, 31, 2622 (1931).

Chapter 35

The Lethal Action of Ultraviolet Rays and Sterilization

It has been known for over a half a century that ultraviolet rays are capable of killing bacteria and molds, but it is only in comparatively recent times that attempts have been made to utilize these results for the practical sterilization of foods, drugs, water and air. The method has, however, definite limitations and at present its use is becoming more and more restricted to surface sterilization of foods, the treatment of relatively expensive materials such as certain pharmaceutical preparations and the irradiation of air in operating rooms and hospital corridors. Studies of the mechanism of the lethal action are important in that they offer a method of attack on some unsolved problems of physiology and pathology.

EARLY HISTORY

As early as 1877, Downes and Blunt¹ discovered the bactericidal action of light on a mixture of organisms encountered in putrefying substances. They showed that rays of short wave-lengths are responsible for the lethal effects, and that these rays are capable of sterilizing either moist or dry organisms. They ascribed the action to a direct effect upon the organisms rather than to effects upon the surrounding media. They were in error, however, in concluding that the presence of oxygen is essential for bactericidal action. This error persisted a long time, being repeated and emphasized by Roux in 1887,² until it was corrected by Ward in 1892.³ Studies were made of the effect of irradiation upon a number of microorganisms by Arloing⁴ and by Duclaux (1885). Ward showed that, although some bactericidal action is exerted by the visible spectrum upon the anthrax bacillus, the most intense lethal effects are due to the ultraviolet rays which fail to penetrate glass. Ward suggested that the carbon arc might be used for the disinfection of small enclosed spaces, such as railway cars.

Other workers added a number of features of physical interest. Such features as the applicability of the inverse square law for the falling off of the intensity of the source with respect to distance, the comparative efficacy of intermittent and continuous irradiation, the effects of temperature and the like, attracted the attention of many workers, particularly of Henri and his collaborators. The general outcome of this work was the realization that physical or photochemical changes were involved which were in some manner dependent upon the absorption of the effective radiations by the organisms.

Ambitious attempts to replace the rather qualitative generalizations of their predecessors by a more quantitative statement of data were made by Bie and Bang in Finsen's laboratory. Each of these observers measured and recorded the energies to which the organisms were subjected in their experiments. Although their work was largely confined to the visible spectrum, it indicated that the bactericidal effect increases sharply as the wave-lengths employed are decreased. Only by the use of long exposures was any germicidal effect obtained by the use of light of the middle range of the visible spectrum. The most valuable contribution of Bie was the introduction of the use of liquid absorption filters to isolate particular spectral regions.

Bang improved the technique by eliminating the heating infrared rays, and extended the measurements into the ultraviolet by the use of quartz. A hanging drop of the

¹ Downes, A., and Blunt, T. P., *Proc. Roy. Soc.*, 26, 488 (1877).

² Roux, E., *Ann. Inst. Pasteur*, 1, 445 (1887).

³ Ward, H. M., *Proc. Roy. Soc.*, 52, 393 (1893); 53, 23 (1893); 54, 472 (1893).

⁴ Arloing, S., *Compt. rend.*, 100, 378 (1885); 101, 511 (1886).

bacterial suspension on the lower surface of a quartz plate was exposed to radiations passing through the quartz. The plate formed the lid of a small quartz chamber, the temperature of which was maintained constant by a thermostatically controlled water jacket. Some of the observations indicated not only that the killing may be very rapid when ultraviolet light is employed, but also that the age of the organism and the temperature at which the irradiation is conducted exert an influence on the results. For example, at 30°C., a culture of *B. prodigiosus* three hours old was killed in 60 seconds, but a culture ten to fifteen hours old required 210 seconds. At 45°C., a three-hour culture was killed in fifteen seconds. This indicated that the reaction underlying the lethal mechanism possesses a positive temperature coefficient.⁶

Bang⁷ also presented a curve for the relative effectiveness of various wave-lengths, consideration of which is reserved for a later section.

In 1903, Bernard and Morgan, working in MacFayden's laboratory at the Lister Institute, made a series of experiments which indicated that⁸ the bactericidal action is practically confined to the region between 3290 and 2265A. By means of a quartz spectrograph, the spectrum of a carbon arc was thrown upon an agar plate superficially inoculated with a culture of *B. coli communis*. After a definite time the plate was incubated. Only that part of the surface which had been exposed to the rays from 3287 to 2265A showed any sign of bactericidal action. Later workers refining on the technique have fixed these limits somewhat differently. Bernard and Morgan found also that the cadmium and the iron arcs were more efficient than the carbon arc.

The active rays were completely arrested by thin films of agar media. The reader is reminded that an agar medium is not a simple gel of agar agar, but contains added proteins and sometimes sugar. These added foodstuffs exert a considerable filtering action. Similar results with a thin membrane of human epidermis stretched as a filter showed that it could not be hoped to sterilize pathogenic organisms located beneath the surface of the skin.

BACTERICIDAL SPECTRAL REGIONS ACCORDING TO EARLIER OBSERVERS

The majority of workers have found the region of bactericidal activity to lie between the wave-lengths 2960 and 2100A. Thus Newcomber,⁹ working with the bacillus of typhoid fever, gives the effective limits as 2800 to 2100A with no action at 2970A. Browning and Russ, using agar¹⁰ surface cultures, a tungsten lamp, and a quartz spectrometer, reported 2960 to 2900A as bactericidal rays, with a maximum action at 2800 to 2540A. Cernovodeanu and Henri,¹¹ using a Cooper-Hewitt lamp and bacterial emulsions, found a maximum at about 2800A; Mashimo,¹² using agar surface cultures and a quartz spectrometer, found the bactericidal range to be from 2950 to 1860A with a maximum at 2750A. Bayne-Jones and von der Lingen¹³ give 3500 to 1856A. Bang,¹³ using a carbon arc at 30 amperes, found the maximum action to be produced by the wave-length 2500A.

The differences reported may be caused by variations in technique, especially the following: surface cultures can be killed by rays of less penetration, that is, of longer wave-length, than are needed for emulsions. This effect is reversed when the emulsion is agitated during irradiation. Arcs between different electrodes vary in their spectral energy distributions. Temperature and hydrogen ion concentration may affect the results.

⁶ See also Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29; *Chem. Abs.*, **1**, 1029, (1907). Contra: Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52, 549 (1910).

⁷ Bang, S., *Mitteilungen aus Finsen's Medisins Lysinstitut*, **9**, 164 (1905).

⁸ Bernard, J. E., and Morgan, H., *Brit. Med. J.*, Nov. 14, 1903, *Proc. Roy. Soc.*, **72**, 126 (1903).

⁹ Newcomber, H. S., *J. Exp. Med.*, **26**, 841 (1917).

¹⁰ Browning, C. H., and Russ, S., *Proc. Roy. Soc.*, **110**, 33 (1917).

¹¹ Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910).

¹² Mashimo, T., *Mem. Coll. Sci. Kyoto*, **4**, 1 (1919); *J. Sci.*, **161A** (1921); *Chem. Abs.*, **15**, 1146 (1921).

¹³ Bayne-Jones, S., and von der Lingen, J. S., *Bull. Johns Hopkins Hosp.*, **34**, 11 (1923); cf. Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).

¹⁴ Bang, S., cited by Henri, V., *Compt. rend.*, **155**, 315 (1912).

On the other hand Bazzoni¹⁴ reported that the full radiation from light source emitting wave-lengths shorter than 2500A will kill bacteria, but that isolate radiations between the limits of 2500 and 2800A will not affect bacteria in a dro of water in an exposure of an hour. He states further that several hours' exposur is needed to kill bacteria with rays of wave-lengths between 2200 and 2250A eve when their intensity is the same as that of the rapidly destructive total radiatio of the same source. These findings are in contradiction with those of many subse quent workers who found bactericidal action even in narrow bands sharply isolate by a quartz spectrometer.

Since little was known regarding the distribution of intensities in the lines o the tungsten arc employed by Browning and Russ, Burger¹⁵ repeated the experi ment, using a mercury arc as the light source, and was able to demonstrate som correlation between the intensities of the lines within the lethal region and thei relative killing effects.

In order to determine the practicability of exposing fruit to ultraviolet rays i order to destroy mold spores, Coblentz and Fulton at the Bureau of Standards con ducted an investigation of the effects of various wave-length regions upon culture of *Staphylococcus aureus*. In commenting upon the culture spectrogram of Brown and Russ (see Figure 132), they stated that the sharp termination of the germicida action in the short wave-length region may have been due to absorption of thes rays in the instrument employed.

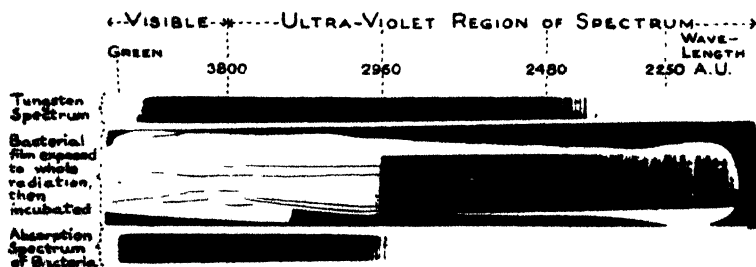


FIGURE 132. Plate of Bacteria Exposed by Spectrograph by Browning and Russ.

Coblentz and Fulton were unable to detect any effect on growth produced by irradiating agar before seeding it with the cultures, unless very high light intensities were used. The absorption spectrum of the bacterial emulsion extended from 2960 to 2100A and coincided with the spectral range of germicidal action. Slight differences in the wave-lengths effective for killing different organisms were found. Thus for *B. coli*, the range for lethal effects extended from 2960 to 2200A and for *B. typhosus* from 3000 to 2100A, and for *Staphylococcus aureus* the range of greatest germicidal action extended from 2960 to 2380A. It may be noted that in the experiments of Baynes-Jones and van der Lingen in which the long wave length threshold was found at 3500A, the cultures were exposed to the sun for three hours. Coblentz and Fulton employed a series of mica screens of various thicknesses for isolating particular regions, the mica having a maximum absorption near 2600A. They found germicidal action even at 3650A, but very prolonged exposures were required when wave-lengths between 2970 and 3650A were used.

¹⁴ Bazzoni, C. B., *Am. J. Public Health*, 4, 975 (1914).

¹⁵ Burger, G., *Bull. Basic Sci. Research*, 2, 46 (1928).

The lethal action of rays shorter than 2800Å was at least ten times more rapid than that of those longer than 3050Å, in spite of the much lower intensity of the shorter rays. Intermittent exposure had the same effect as continuous exposure for the same total time of exposure, that is, the action is cumulative. These authors estimated the energy between 1700 and 2800Å required to kill a single bacterium to be of the order of 19×10^{-12} watt.¹⁶

INTERPRETATIONS OF THE LETHAL MECHANISM

Bedford¹⁷ attempted to revive an earlier theory of an indirect lethal mechanism in which it was assumed that the organisms are killed by the action of hydrogen peroxide formed by the ultraviolet rays. Such a mechanism would require a wave-length dependence similar to that for the production of hydrogen peroxide, which differs from the results described in the preceding paragraphs. Furthermore, such a mechanism is inadequate to account for the observed facts (described in a subsequent paragraph) regarding the relative efficiencies of various wave-lengths operating at the same intensity. Moore and Webster¹⁸ attributed the germicidal power of sunlight to the production of formaldehyde.

Proks¹⁹ claimed that irradiation of the culture medium previous to inoculation lessens its ability to support growth. It may be recalled that Coblenz and Fulton had observed a similar result after prolonged irradiation of agar. Blank and Arnold²⁰ state that radiations of 2537Å change agar or agar-water gels so that they no longer support the growth of *B. subtilis*. There is formed a nonvolatile, thermostable material capable of diffusing through the gel. A similar inhibiting effect results from the addition to the medium of an irradiated solution of a carbohydrate. In confirming these results, Baumgartner²¹ notes that irradiation of carbohydrates is accompanied by a marked production of acid, approximately half of which is formic. Neutralization restores the ability of the medium to support growth. Further confirmation is reported by Pratt.²² Calabek²³ believed that the Höhensonne lamp, as well as natural solar rays, lowers the swelling capacity of agar disks to an extent dependent upon the time of irradiation. The maximum decrease was achieved after an illumination of 146 minutes on one side of the disk, the subsequent swelling in water reaching only 1525 per cent instead of the normal 3200 per cent. The action of the radiations was practically limited to the extreme layers of the gel, decreasing to about zero at 0.08 mm. below the surface. Kersten and Dwight²⁴ find that irradiation of dry agar decreases the viscosity and pH of the sol subsequently made.

Such effects on the medium have, however, little to do with the mechanism by which organisms on the surface of a plate are killed within a few seconds of exposure to ultraviolet rays. In this case, it is necessary to seek for a direct action of the rays upon the organisms. To determine which of the chemical constituents of the organisms absorb the light in the primary process, subsequent

¹⁶ Coblenz, W. W., and Fulton, H. R., *Bureau of Standards Sci. Papers*, 19, 495, 641 (1924).

¹⁷ Bedford, T. H., *Brit. J. Exptl. Path.*, 8, 437 (1927).

¹⁸ Moore, B., and Webster, T. A., *Proc. Roy. Soc.*, 90, 168 (1918).

¹⁹ Proks, J., *Lait*, 13, 331 (1933); *Chem. Abs.*, 27, 3233 (1933). To eliminate effects on the media, D. G. Sharp atomizes broth cultures into air where they may be irradiated. *J. Bact.*, 35, 589 (1938).

²⁰ Blank, I. H., and Arnold, W., *J. Bact.*, 30, 507 (1935).

²¹ Baumgartner, J. G., *J. Bact.*, 32, 75 (1936).

²² Pratt, E. L., *J. Bact.*, 32, 613 (1936).

²³ Calabek, J., *Protoplasma*, 3, 17 (1927); *Chem. Abs.*, 22, 3896 (1928).

²⁴ Kersten, H. J., and Dwight, C. H., *J. Phys. Chem.*, 41, 687 (1937).

workers have compared the absorption spectra of various cellular components with the spectral regions of greatest lethal activity.²⁵

Following a suggestion of Henri²⁶ that the abiotic power of various wave-lengths parallels their absorption by proteins, Harris and Hoyt²⁷ found that *B. subtilis*, irradiated by ultraviolet filtered through a 1-per cent tyrosine solution, survived exposures of forty minutes. On direct exposure, the organisms were killed in 150 seconds. Similar results were obtained with *Staphylococcus aureus* and *B. mucosus capsulatus*. These experiments do not, however, afford proof that the lethal action of ultraviolet rays is to be attributed to an effect upon the aromatic amino- acids of the proteins. This work had a considerable influence on the opinions of biologists and for a time the effects of radiations upon the proteins were perhaps overemphasized.

In 1914, Henri stated²⁸ that the abiotic power of ultraviolet light was the result of photochemical action on certain molecular groupings of the protoplasm and, especially, the cell nucleus. In 1916, Galeotti²⁹ showed that the reproductivity of *B. typhosus*, *B. paratyphosis* and *B. subtilis* could be destroyed by less intense ultraviolet light without causing them to lose their motility, an indication that the first locus of attack is upon some material associated with cell division. Bovie and Hughes³⁰ found that exposures of *Paramecium caudatum* only one-thirteenth as long as those necessary to produce cytolysis were sufficient to inhibit all division.

Some observers have described changes wrought in bacteria by non-sterilizing doses of ultraviolet rays. Henri³¹ claimed to have produced two new forms from anthrax bacilli in this manner. Eberson³² believed the irradiation of certain types of meningococci to diminish their virulence and increase their antigenic power. However, attention has not been devoted to any extent to this type of ultraviolet effect.

In 1928, Gates published a brief note stating that³³ "the reciprocal of the bactericidal energy curves matches the absorption curves for certain of the nucleoproteins—cytosine, thymine and uracil—more closely than it does those for various aromatic acids such as tyrosine, tryptophane and phenylalanine, suggested by Harris and Hoyt." That derivatives of the nucleic acids should be concerned agrees well with the observations that it is the reproductive function which is first destroyed by the action of ultraviolet rays. It must be remembered that in most experimental work the criterion of death based upon the counting of colonies which grow in media inoculated by irradiated organisms is really a criterion of the failure of cell division to occur at the normal rate.

Gates³⁴ employed a quartz monochromator to separate the wave-lengths emitted by a quartz mercury arc, and measured the intensity at the exit slit by means of

²⁵ Rahn, O., [J. Gen. Physiol., 13, 179, 395; 14, 315] has assumed that each cell contains one or several extremely sensitive molecules, the destruction or inactivation of any one of these preventing the multiplication of the cell. He believes that it may be necessary for more than one molecule to be destroyed in order that a yeast cell may be killed. In the case of the spores of the mold *Botrytis cinerea*, the number of reacting molecules is thought to be greater than one; and in the flagellate *Colpidium*, Rahn believes that two molecules must be destroyed before mobility ceases.

²⁶ Henri, V., *Compt. rend. soc. biol.*, 73, 323.

²⁷ Harris, F. I., and Hoyt, H. S., *Pathology*, 2, 245 (1919); *Chem. Abs.*, 13, 2384 (1919).

²⁸ Henri, Mme., *Compt. rend.*, 158, 1032 (1914).

²⁹ Galeotti, G., *Ann. Inst. Pasteur*, 30, 49 (1916); *Chem. Abs.*, 10, 2358 (1916).

³⁰ Bovie, W. T., and Hughes, D. M., *J. Med. Research*, 23, 223 (1918).

³¹ Henri, Mme., *Electrical Review*, 74, 768 (1914).

³² Eberson, P., *J. Immunol.*, 5, 345 (1920); *Chem. Abs.*, 14, 3273 (1920).

³³ Gates, F. L., *Science*, 58, 479 (1928).

³⁴ Gates, F. L., *J. Gen. Physiol.*, 13, 231 (1929).

thermopiles. A suspension of *Staphylococcus aureus* was flowed over an agar plate and exposed at the exit slit. After the exposure, this was covered with another layer of agar and incubated. The area counted coincided with the area of the thermopile junction. The energies applied were varied by altering the times of exposure. From a large number of experiments, smooth curves were obtained for the variation in the per cents of bacteria killed with variation in the logarithms of the available energies expressed in ergs per square millimeter.³⁵ The curves were so similar as to indicate that the reaction at any one wave-length is typical of them all. The form of the S-shaped curves is one frequently encountered in experimental biology. Four conclusions were drawn from this work.

1. No bacteria succumb in the initial period of exposure. The energy incident during this initial period is between 6 and 7 per cent of that required to kill all of the organisms.

2. After this period, between 20 and 30 per cent of the organisms were found to be destroyed by less energy than would be predicted from the rate of destruction of the remainder of the organisms. They seem to be less resistant than the rest.

3. A considerable proportion of the remaining bacteria (about 70 or 80 per cent of the total number) succumb along an energy gradient that bears an exponential relationship to the lethal effect, i.e., a straight line. In other words, the middle portion of the curve may be reproduced by the equation describing the course of a monomolecular reaction.

4. In the final period there are remaining a number of organisms which are killed only by an excess of energy.

The second feature discussed above is attributed to the fact that young bacteria are less resistant than are older, resting organisms, a fact which had been demonstrated by Bang.³⁶ Gates was of the opinion that there was no evidence in his work that sublethal doses exerted any stimulating effect on the subsequent multiplication of bacteria, although this had been claimed by Browning and Russ.³⁷ This may have been due to the fact that when few bacteria survive in the middle of an exposed area, or when relatively few are left at the edges where the intensity of the radiation falls away, the colonies they produce are always much larger than those in the more crowded areas of the plate. The reason for the more active multiplication and consequent large colonies under these circumstances Gates believed to be merely that the nutrient substances per colony are not so limited, and also that waste products do not accumulate so rapidly.

One point of view regarding the nature of the lethal process disregards the features indicative of individual differences in the resistance of the organisms and considers the curve evidence for a fundamental monomolecular reaction underlying the process. Another point of view, to which Gates inclined, regards the course as determined by probability considerations and suggests that it should be compared with the mortality curves of insurance statistics. The similarity of the middle portion of the curve to that of monomolecular reactions is ascribed to a coincidence in the distribution of the resistance factors.

Gates showed³⁸ that wide variations in the intensities of incident ultraviolet energy (from 21.6 to 5.6 ergs per sq. mm.) were not accurately compensated for by making the appropriate changes in the times of irradiation. Thus the Buensen-

³⁵ Hertel, E., [*Z. allgem. Physiol.*, 4, 1 (1904); 5, 95 (1905)] had made a beginning in this type of work, but he had reported only on the effects of six lines. Compare also Bang, S., *loc. cit.*

³⁶ Bang, S., *Mitteilungen aus Finsen's Lichtinstitut*, 2, 1 (1901).

³⁷ Browning, C. H., and Russ, S., *Proc. Roy. Soc.*, 110, 33 (1917).

³⁸ Gates, F. L., *J. Gen. Physiol.*, 13, 249 (1929).

Roscoe reciprocity law does not hold strictly. The deviations were most marked with young organisms, metabolically and genetically active.

An exposure of thirty minutes at 3340 or 3660Å failed to reduce the subsequent formation of colonies. Although the first experiments with 3130Å indicated some bactericidal action, in later ones in which stray reflected light was more rigorously excluded, even very large incident energies had no appreciable effect.

No attempt was made to determine the short wave-length limits of lethal action. Weak lines at 2340, 2300 and 2250Å required such long exposures that it was possible to establish only the middle portion of the curve of lethal action. Lyman³⁹ showed the bactericidal effects of radiations shorter than 1860Å and Bovie⁴⁰ extended the lower limit to 1250Å by the use of a hydrogen discharge tube and fluorite windows.

The lethal action has a temperature coefficient of 1.1, in agreement with the observations of Baynes-Jones and van der Lingen. Gates was unable to confirm the results of Thiele and Wolf,⁴¹ and of Wiesner⁴² who found an increase in temperature to extend the bactericidal zone toward the longer wave-lengths.

Variations in the pH of the medium between 4.5 and 7.5 were without influence on the lethal action, but at pH 9 and 10 there was a slight but definite increase in bacterial sensitivity. Plane-polarization of the incident ultraviolet light had no effect upon bactericidal action.⁴³

Although the killing curves obtained by the use of different wave-lengths are similar in form, they lie at very different energy levels.⁴⁴ Thus energy required to kill half of the exposed organisms ranges from 3150 ergs per sq. mm. at 3020Å to only 88 at 2660Å. The latter wave-length has been reported to be optimum for killing organisms, longer or shorter ones requiring more incident energy. On plotting against the wave-lengths as abscissae the reciprocals of the energies required at various wave-lengths to kill half of the organisms, the curves showed a maximum at 2660Å, a minimum near 2400Å and another maximum beyond 2300Å. A similar curve was obtained for *B. coli*.⁴⁵ Absorption curves of thin films of the organisms pressed between quartz plates were strikingly similar to the curves for the reciprocals of the energies required.

Comparatively few references are available on the absorption of the materials of the cell nucleus. Dhéré in 1906 stated that 4-methyluracil exhibits an absorption band between 2346 and 2801Å. Since this was very similar to the absorption observed in the case of nucleic acid, he attributed the absorption spectrum of the latter to its pyrimidine and purine components. Holiday⁴⁶ more recently reported quantitative data on the absorption spectra of several purines.

Heyroth and Loofbourow⁴⁷ gave absorption curves for a number of purines and pyrimidines and showed that the absorption of thymonucleic acid may be represented as the summation of the molar extinction coefficients, at least at 2600Å of

³⁹ Lyman, T., "Spectroscopy of the Extreme Ultraviolet," Longmans, Green and Company, pp. 1-3, 2nd ed., London, 1928.

⁴⁰ Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).

⁴¹ Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29, *Chem. Abs.*, **1**, 1029 (1907).

⁴² Wiesner, R., *Arch. Hyg.*, **61**, 1 (1907).

⁴³ Bhatnagar, S. S., and Lal, R. B., [*Nature*, **117**, 302 (1926)] had previously suggested as a result of preliminary experiments on *B. typhosus* and *Vibrio cholerae* that bacterial life is favorably affected by polarized light as compared with ordinary light of equal intensity.

⁴⁴ Gates, F. L., *J. Gen. Physiol.*, **14**, 31 (1930). Cf., however, Herçik, F., *J. Gen. Physiol.*, **20**, 589 (1937).

⁴⁵ For *E. coli*, V. Henri finds the maximum bactericidal action at 2750Å. *Festschr. Zangger*, **2**, 792 (1935); *Ber. ges. Physiol. exptl. Pharmacol.*, **86**, 363; *Chem. Abs.*, **31**, 6683 (1937).

⁴⁶ Holiday, E. R., *Biochem. J.*, **24**, 619 (1930).

⁴⁷ Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931); **56**, 1728 (1934).

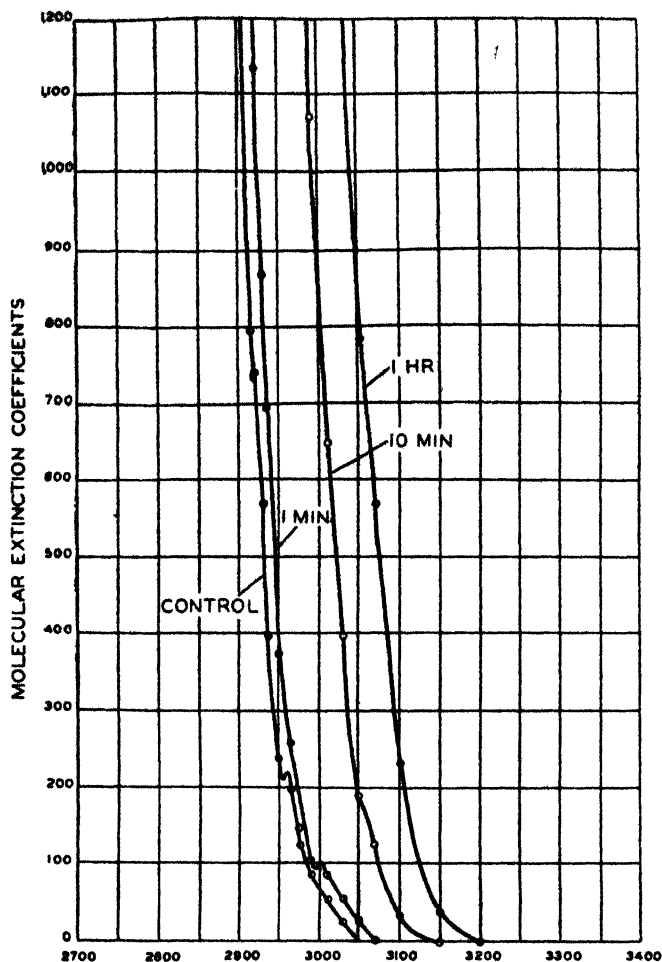


FIGURE 133. Absorption of Uracil at one gram per liter, Showing Effect of Irradiation with Full Ultraviolet (Heyroth and Loofbourow, *Journal American Chemical Society*).

adenine, guanine, cytosine and thymine. They advanced arguments for viewing their absorption data as supporting the hypothesis of Gates that it is energy absorbed by these cellular components which is concerned in the lethal mechanism.⁴⁸ The absorption of the typical pyrimidine, uracil, in a concentration roughly comparable to that estimated as present in the cell nucleus, rises very abruptly and rapidly at about 2950Å. This is the wave-length found by many workers to represent the approximate lethal threshold for the rapid action of ultraviolet rays on bacteria. (See Figure 133.) The concentration of one gm. per liter was chosen for these measurements because of the following considerations. Assuming for tubercle bacilli a water content of 70 per cent and in the dried material a fat content of 40 per cent, the work of Johnson and Brown, who obtained 7.7 gms. of a

⁴⁸ Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Sci. Research*, 5, 13 (1933).

nucleic acid from 436 gms. of dried and fat-free bacteria, would indicate the presence of at least 0.3 per cent of this nucleic acid in the fresh organisms.⁴⁹ Assuming for this tuberculinic acid a molecular weight approximately that of thymonucleic acid, the absorbing nitrogenous bases would be at least one two-hundredth per cent of the weight of the fresh bacteria. A solution of one gm. per liter of any one of the absorbing bases would be of the same order of concentration as in the fresh bacteria.

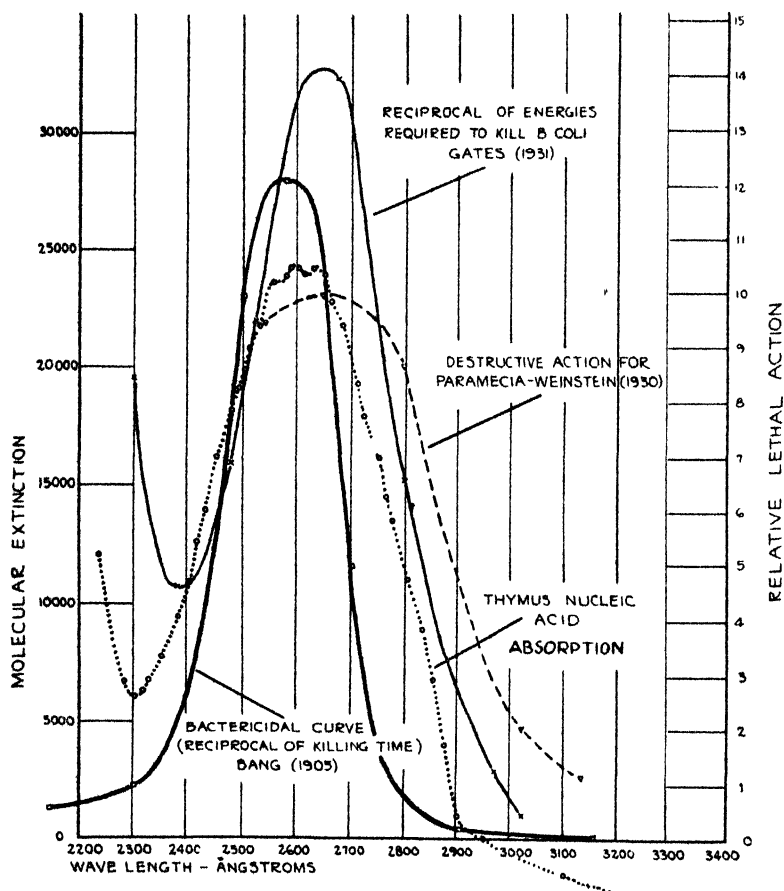


FIGURE 134. Comparison of Lethal Action of Ultraviolet and Absorption of Nuclear Materials. (Heyroth and Loofbourow, *Bull. Basic Sci. Research.*)

It is apparent that the absorption curve of these pyrimidine and purine bases in concentrations comparable to those found in the cell corresponds closely to the lethal threshold for the killing of microorganisms. As indicated by the figure, this long-wave absorption curve for high concentrations of the nuclear materials moves toward still longer wave-lengths during the irradiation of these substances with unfiltered ultraviolet light. This produces a filtering effect which tends to

⁴⁹ Johnson, T. B., and Brown, E. B., *J. Biol. Chem.*, 54, 721 (1922).

screen the unchanged substances from the destructive action of the radiations. It is a matter of extreme interest that this occurs particularly with respect to the shortest wave-lengths that may be found in the solar spectrum as available on the surface of the earth.

The point of maximum absorption by most of these pyrimidine and purine bases and by nucleic acid itself lies near 2600Å.⁵⁰ To make clear the similarity between the forms of these absorption curves and those of the reciprocals of the energies required for killing, and interpreted by Gates as the curve for the absorption by the sensitive materials in the cells, curves have been plotted in Figure 134. These compare the data of Gates, of Bang and of Weinstein (for the killing of *Paramecia*) with the⁵¹ absorption curve of nucleic acid. Both the nucleic acids from yeast and from thymus glands have the same type of absorption curve.

Only in those organisms in which the nuclear material is diffused throughout the cell (bacteria and yeasts) or in which the nucleus is unprotected by a thick layer of cytoplasm should the absorption by nucleic acid be expected to play a predominant role in the lethal action. Proteins may play a more important role in the effects on cells such as the protozoa in which the nucleus is more adequately protected by a thicker surrounding layer of protoplasm. The thickness of such a cytoplasmic layer in many of the protozoa may exceed many times the entire diameter of bacteria. Indeed, in the case of such large cells there is some evidence to show that the optimum lethal action takes place rather closer to 2800Å, the position of the absorption maximum of the proteins, than to 2600Å, the position of the maximum absorption by nucleic acid. A quantitative comparison of the absorption of equally concentrated protein and nucleic acid solutions shows that a far greater proportion of the incident energy is absorbed at their respective maxima by the nucleic acid than by the proteins. The absorption of the proteins in this region is due (see the preceding chapter), to the tyrosine, tryptophane and other aromatic amino- acid components. Not only are the molecular extinction coefficients of tyrosine (approximately 2000 cm.⁻¹), and of tryptophane (5000 cm.⁻¹) at 2800Å lower than those found at 2600Å for adenine (10,300 cm.⁻¹), guanine (12,000 cm.⁻¹), cytosine (6100 cm.⁻¹), thymine (9000 cm.⁻¹) and uracil (9100 cm.⁻¹), but their proportions in the molecules of proteins (rarely over 2 per cent) are much less than those of the absorbing nitrogen ring compounds in the molecules of nucleic acids.

Relatively little is yet known as to the nature of the changes induced in the pyrimidines by the action of ultraviolet rays. The absorption spectrum changes during irradiation in the manner indicated in Fig. 135.⁵² The molecular extinction curve of uracil is given in the upper heavy curve (concentration of 10 mg. per liter). During the first few minutes of irradiation with full ultraviolet light from a mercury arc there is a definite rise in absorption in the region from 2200 to 2300Å and also in the region of wave-lengths longer than 2900Å. During the later periods of irradiation, the absorption of the head of the band decreases. In the case of uracil this change occurs after fifteen minutes of exposure at 2 cm. from a Victor water-cooled arc. For a time the rise in absorption at both legs of the curve continues although the absorption at the center of the band is diminishing. After about fifteen minutes, however, the absorption between 2200 and 2300Å also begins to decrease, although that of the rays of wave-length longer than 2900Å continues to increase for three hours and then decreases. If the radiation

⁵⁰ Heyroth, F. F., and Loofbouroow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).

⁵¹ Weinstein, I., *J. Opt. Soc. Am.*, **20**, 433 (1930).

⁵² Heyroth, F. F., and Loofbouroow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).

is sufficiently prolonged, practically all selective absorption is lost, the absorbed energy causing photochemical changes which destroy the pyrimidines. In the case of nucleic acid, an irradiation of an hour caused but negligible change between 2500 to 2900A, but in the region near 2300A the extinction coefficients increased nearly 45 per cent. The position of the minimum shifted slightly toward longer wave-lengths during this period. On more prolonged irradiation the absorption at the head of the band decreased.

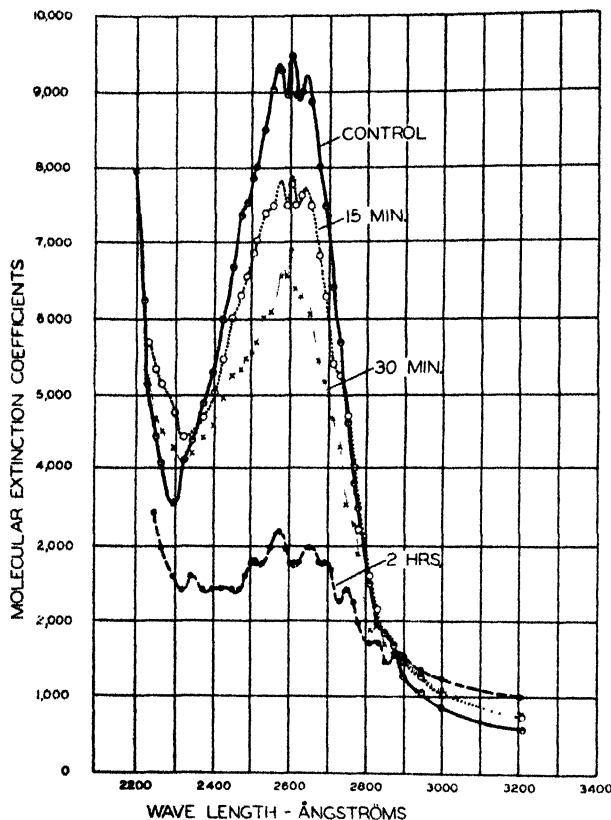


FIGURE 135. Effect of Ultraviolet Irradiation upon the Absorption Spectrum of Uracil. (Heyroth and Loofbourov, *Journal American Chemical Society*.)

The mechanism underlying these changes is as yet unknown. There may be either a rupture of the ring with the production of diacetic products of the nature of urea and open-chain three-carbon compounds, or there may be a gradual saturation of the ring. Bass has shown that thymine, after twelve hours of ultraviolet irradiation in the presence of oxygen and ferrous salts, yields urea and pyruvic acid.⁵³ Lieben and Getreuer,⁵⁴ state that no ammonia is liberated during the irradiation of uric acid, xanthine, uracil, alloxan, hydantoin and α -hydroxynicotinic acid. There is, however, evidence of an increase in free amino- groups

⁵³ Bass, L. W., *J. Am. Chem. Soc.*, 46, 190 (1924).

⁵⁴ Lieben, F., and Getreuer, V., *Biochem Z.*, 259, 1 (1933).

indicative of a rupture of the ring. Sodium nucleate is relatively resistant to rupture. Histidine, proline, guanine, pyridine and nicotinic acid evolve ammonia. In these cases the destructive effect apparently is hastened by oxygenation, but the latter is not essential to the change.

It was suggested by Heyroth and Loofbourow that the early change might involve the formation of a compound of the type of α -isouracil described by Tafel and Houseman.⁵⁵ Since the formula proposed by those workers involved the presence of a hydroxyl group in position five, and since Johnson and Johns⁵⁶ had concluded that the ability of pyrimidine compounds to reduce phosphotungstic acid in alkaline solution depends on the presence of amino- or hydroxyl groups in this position, Heyroth⁵⁷ investigated the effect of irradiation upon the ability of uracil to reduce this reagent. It was found that irradiation of a uracil solution induces a photochemical change resulting in the formation of a substance or substances capable of reducing an arsenophosphotungstic acid solution. The rate of change was greatest early in the irradiation. The observation of the occurrence of this reaction may be of aid in the interpretation of certain findings in the physiology of irradiation. Clinical observations of an 80-per cent increase in the blood uric acid and purines have been reported by Wiener⁵⁸ to occur in patients undergoing phototherapy. Koch and Reed⁵⁹ reported a 38-per cent increase in the blood uric acid of a dog during irradiation with a carbon arc for an hour and a half. The blood was irradiated while flowing through quartz tubes introduced into the circulation. These authors did not attribute the increased values to the formation of uric acid but instead to the presence of some substance giving a similar reduction of the uric acid reagent (phosphotungstic acid) used for the determination of the so-called blood uric acid. Dillman⁶⁰ could not obtain the increase when the blood was irradiated *in vitro*. He also noted that irradiation of uric acid destroys its ability to reduce phosphotungstic acid. The observations on uracil suggest the purine or pyrimidine nucleosides of the blood as a possible source from which such a reducing substance might be formed during irradiation. Pincussen and Flores⁶¹ by experiments *in vitro* attempted to learn something of the fate of nucleins exposed to radiations. Specimens of nucleic acid were exposed to the rays of a Nitra lamp, the heat rays being removed by a water filter. Eosin and dichloroanthracene were tested as sensitizing agents, and the changes in the specific rotation of the solution of nucleic acid were followed. A splitting of the acid was pronounced without sensitizer or in the presence of eosin, but was not detected in the presence of the anthracene compound. The nucleic acid-splitting enzymes did not appear to be increased when animals were irradiated.

Ultraviolet photomicrographs of the chromosomes of *Drosophila* in various fluid reagents have been given by Hellström, Brandt and von Euler.⁶²

Peptization of cell colloids was obtained when a sharp pencil of ultraviolet light was passed into the macronuclei of *Paramecium caudatum*, *Spirostomum ambiguum*, and *Amphileptus clapedei*.⁶³ Microscopic ultraviolet absorption methods have been employed to follow the distribution of nucleic acid in tissues during the proc-

⁵⁵ Tafel, J., and Houseman, P. A., *Ber.*, 40, 3743 (1907).

⁵⁶ Johnson, T. B., and Johns, C. O., *J. Am. Chem. Soc.*, 36, 970 (1914).

⁵⁷ Heyroth, F. F., *Bull. Basic Sci. Research*, 4, 128 (1932).

⁵⁸ Wiener, H., *Klin. Wochschr.*, 3, 936 (1924).

⁵⁹ Koch, F. C., and Reed, C. I., *Am. J. Physiol.*, 75, 351 (1925).

⁶⁰ Dillman, L. M., *J. Lab. Clin. Med.*, 17, 44 (1931).

⁶¹ Pincussen, L., and Flores, A., *Biochem. Z.*, 126, 86 (1921). See also Chapter 33.

⁶² Hellström, H., Brandt, K., and von Euler, H., *Svensk Kem. Tids.*, 47, 249 (1935); *Mikrochemie, Festschr. Hans Molisch*, 2093 (1936).

esses of mitosis and glandular secretion.⁶⁴ In the large chromosomes of *Stenobothrus* spermatocytes, the absorption curves correspond to those of a 15-per cent solution of thymonucleic acid. Chromosomes are built up of alternating nucleic acid segments and protein segments.⁶⁵

Interesting observations of another type relating to the effect of ultraviolet rays in killing *Escherichia coli* have been reported by Lisse and Tittsler.⁶⁶ By the use of either Northrop-Kunitz or Falk capillary electrophoresis cells, they found that irradiation, if of sufficient duration, produces a decrease in the negative charge of the organism. With the former type of cell they found some indication of an initial stimulative action of the ultraviolet radiations which made itself felt in an increase of the negative charge. This could not, however, be observed with the Falk capillary cell. Short irradiations which merely stimulate or injure the cells permit a return of the electrokinetic velocity toward its normal value, but prolonged lethal irradiation produces a lasting effect. The sequence of decreasing electrophoretic velocities is the same as that of increasing susceptibility to agglutination except in the case of very long or very short irradiations. The interposition of a Corex A filter causes a practical disappearance of this sequence of agglutinability. Irradiation by a carbon arc also produced lysis which was the greater the longer the irradiation. Irradiation produced an increase in the pH of an aqueous suspension of cells, the original pH of which was approximately 6.1. With 500-watt Mazda bulbs as the light source there was eventually a reduction of the charge and evidence of lysis indicated by a clearing of the suspension, but much longer times of irradiation were required than when ultraviolet light was used. Norton⁶⁷ also suggested that the changes suffered by bacteria on exposure to ultraviolet rays may be accompanied or perhaps preceded by changes in the electrical charges borne by the bacteria.⁶⁸

Gärtner⁶⁹ finds the agglutinability of bacterial suspensions to be increased and the zone of acid agglutination widened by irradiation, although the acid zone is narrowed by prolonged exposures. Basic dyes agglutinate irradiated bacteria in lower concentrations. The pH is increased and the acid-binding power decreased. Agglutinability with antiserum is decreased.

Pincussen and Gutfeld⁷⁰ studied the influence of salt solutions on the killing of various organisms by light. With *Staphylococcus aureus*, the killing effect in calcium chloride solutions was about three times that obtained in distilled water, but other salts, including the chlorides of sodium, potassium and magnesium, were without this influence. Calcium chloride had a protective action on the diphtheria bacillus, the action of light being about four times greater in distilled water. Ehrismann⁷¹ studied the effect of various cations in inhibiting the lysis or clearing of suspensions of bacteria. The process is recognized by a decrease in the volume

⁶⁴ Tchakhotine, S., *Compt. rend.*, 202, 778 (1936).

⁶⁵ Caspersen, T., *Skand. Arch. Physiol. Suppl.*, 8, 151 pp. (1936); *Bull. histol. appl. physiol. path. tech. microscop.*, 14, 33 (1937); *Protoplasma*, 27, 463 (1937); Caspersen, T., Hammarsten, E., and Hammarsten, H., *Trans. Faraday Soc.*, 31, 367 (1935).

⁶⁶ Caspersen, T., *Naturwiss.*, 23, 527 (1935).

⁶⁷ Lisse, M. W., and Tittsler, R. P., *Proc. Soc. Exp. Biol. Med.*, 28, 811 (1931).

⁶⁸ Norton, J. F., in Jordan, E. O., and Falk, J. S., "Newer Knowledge of Bacteriology and Epidemiology," Univ. of Chicago Press, 374 (1928).

⁶⁹ For other references to this work, see Lisse, M. W., *Penn. Agr. Sta. Tech. Bull.*, 230, 6 (1928), 243, 6 (1929); 258, 8 (1930); Tittsler, R. P., and Dozois, K. P., *Ibid.*, 258, 28 (1930); Lisse, M. W., Tittsler, R. P., and Sharpless, G. R., *Ibid.*, 276, 4 (1932). The last includes an exhaustive bibliography on the lethal action of ultraviolet rays.

⁷⁰ Gärtner, I., *Z. Immunitäts.*, 80, 493 (1933); *Chem. Abs.*, 28, 5491 (1934); Gärtner, I., and Szathmary, J., *Z. Immunitäts.*, 78, 249 (1933).

⁷¹ Pincussen, L., and Gutfeld, F. V., *Centr. Bakt. Parasitenk.*, 1 Abt., 109 (1928).

⁷² Ehrismann, O., *Z. Hyg. Infektionskrankh.*, 111, 618 (1930); *Chem. Abs.*, 25, 721 (1931).

of the suspended particles or by the appearance of nitrogenous compounds in the surrounding fluid. An accelerated decomposition of the bacterial proteins into amino-acids could not, however, be demonstrated. The following cations inhibit the action in the order indicated: $\text{La}^{++} > \text{Ca}^{++} > \text{Ba}^{++} > \text{Sr}^{++} > \text{Mg}^{++} > \text{Na}^+$ or Li^+ or K^+ . Also an increase in temperature, displacement of the pH to the acid side, the addition of formaldehyde or of mercuric chloride inhibit decomposition. The various bacteria studied could be arranged in a series according to their sensitiveness.

Number of Quanta Per Bacterium Required for Killing. The question has been raised as to the number of quanta which must hit a single organism, which of course is itself a system containing many molecules, in order to kill it. The reasoning involved has been discussed by Wyckoff for killing bacteria by high-velocity electrons,⁷² where it appeared that the absorption of a single high-voltage electron by a colon bacillus was sufficient to cause death.

In the case of the killing by x-rays,⁷³ Wyckoff found that the absorption of a single x-ray quantum of energy sufficed to kill an organism, although only about one in twenty of the absorbed quanta was effective. From this he concluded that within the organism there is some sensitive region the destruction of which leads to death, and that this sensitive "cell" must have a volume less than 6 per cent of the bacterium itself.

The case is somewhat different in the lethal action of ultraviolet rays. Wyckoff⁷⁴ interpreted the results of Gates on *Staphylococcus aureus* as indicating curves of a "multiple-hit-to-kill" type. Since he believed that the tendency of this organism to cling together in chains made it impossible to spread them properly, he repeated the experiments with the more motile *B. coli*. Survival-ratio curves at various wave-lengths when plotted on semilogarithmic paper gave straight lines, indicating an exponential killing rate. This might be due either to a single quantum-hit killing the organism or to a suitable distribution of the sensitivities of the bacteria. The slope of these curves at all wave-lengths less than 3000Å indicated an average number of effective absorptions per bacterium per second of somewhat less than 0.03. From the intensity of the energy and the volume of the bacterium, it could be calculated that for the 2699Å line, the radiant energy absorbed per bacterium per second was 0.99×10^{-6} erg. Since each quantum at this wave-length represents 7.25×10^{-12} erg, the total number of quanta absorbed per bacterium per second was calculated to be 136,000. But of these, less than one (0.03) was effective in causing death. Thus only $0.03/136,000$ or one in 4.19×10^6 of the absorbed quanta was effective. Wyckoff then proceeded to multiply the volume of one bacterium (3.93×10^{-13} cc.) by a fraction $0.03/136,000$ and thus obtained what he considered to be a sensitive volume, which was 9.38×10^{-20} cc. As it could be calculated that this is approximately the volume which might be occupied by an average-sized protein molecule, it was possible to make the suggestion, although with reservations, that the lethal action depends upon an effect upon one protein molecule in the organism. That the explanation was unlikely was indicated by the fact that the millions of non-lethal quanta absorbed per bacterium did not cause any alteration in the growth rate. However this may be, the data indicate for the organism a very low quantum yield. In liquid or solid systems low quantum yields do not necessarily imply the existence of some unusually sensitive substrate molecule or unit cell. Other explanations of the low quantum yield will undoubtedly

⁷² Wyckoff, R. W. G., *J. Exp. Med.*, **51**, 921 (1930).

⁷³ Wyckoff, R. W. G., *J. Exp. Med.*, **52**, 435, 769 (1930).

⁷⁴ Wyckoff, R. W. G., *J. Gen. Physiol.*, **15**, 351 (1932).

be advanced when the photochemical reactions leading to the death of the organism are better understood.

In general, Wyckoff found the energies required to kill half of the organisms at various wave-lengths to be of the same order as those reported by Gates. Like Gates, he found that the greatest effectiveness lies at about 2652A. There are, however, some discrepancies between the energies found by Gates and by Wyckoff, for which no explanation is yet apparent. It is also interesting to note that Wyckoff found at 3132A that the curve for survival-ratios against time could not be indicated on semilogarithmic paper by a straight line with the same accuracy as the curves obtained at other wave-lengths. It seems possible that the mechanism of killing at wave-lengths longer than 2900A is different from that at the shorter wave-lengths.

Evidence for a variation in the resistance of individual cells has occasionally been noted, particularly in the work of Gates previously discussed. Beauverie⁷⁵ finds that the resistance of yeast cells increases in proportion to their glycogen content.

Although all microscopic living forms can be killed by ultraviolet light, they exhibit varying degrees of resistance either inherent and specific to the organism, or extrinsic and due to the conditions of the irradiation. Among themselves bacteria show considerable, and to some extent characteristic, variations of resistance from species to species. But an attempt to employ these variations for the differentiation of bacteria was unsuccessful.⁷⁶ Nogemi⁷⁷ finds that *Es. coli*, streptococci and the cholera vibrio are killed readily and that the tubercle and anthrax bacilli are more resistant. In general spores are somewhat more resistant than vegetative forms.⁷⁸

Sunlight has a deleterious action on cultures of *Brucella abortus*, sterilizing them in three hours. Ultraviolet light has a similar effect.⁷⁹

According to Mayer and Dworski,⁸⁰ a suspension of tubercle bacilli containing 2,750,000 organisms per cc. was killed within four minutes by the absorption of 1.42×10^9 ergs per sq. cm. from unfiltered radiations of the quartz mercury arc. Exposure to an intensity of 5.93×10^6 ergs per sq. cm. per second for 25 minutes did not alter the acid-fast staining qualities of these organisms. When fixed by heat and irradiated for 5 to 25 minutes, the bacilli showed changes indicative of disintegration, since irregularities were observed on staining by the Ziehl-Neelsen method.

Akiyama⁸¹ claims that *Es. coli*, *Sal. typhimurium* and staphylococci in salt solution are more resistant to ultraviolet light when sensitized with their own specific serums than when treated with heterologous immune serums or with normal serum. The bacteria treated with the globulin fraction of the specific immune serums are more resistant than those treated with the albumin fractions of the same serums.

Bacteria killed by ultraviolet light lose a considerable part of their toxicity toward laboratory test animals, but completely retain their antigenic and immunizing characteristics.⁸²

⁷⁵ Beauverie, J., *Compt. rend.*, 199, 81 (1934).

⁷⁶ Browning, C. H., and Russ, S., "Applied Physiology," p. 150, Oxford University Press, 1918.

⁷⁷ Nogemi, Y., *Kitasato Arch. Exp. Med.*, 10, 135 (1933).

⁷⁸ Lagerberg, O., *Z. Immunitäts.*, 28, 186 (1919); *Chem. Abs.*, 13, 2385 (1919).

⁷⁹ Morales-Otero, P., *Puerto Rico J. Pub. Health & Trop. Med.*, 6, 1 (1930).

⁸⁰ Mayer, E., and Dworski, M., *Tubercle*, 13, 500 (1932).

⁸¹ Akiyama, M., *Sri-ikai Med. J.*, 54, No. 5, 840 (1935); *Chem. Abs.*, 30, 3018 (1936).

⁸² Trotskii, V. L., Sviridova, T. A., and Super, L. P., *J. Microbiol., Epidemiol., Immunobiol.*, 15, 519 (1935); *Chem. Abs.*, 30, 4531 (1936).

Recently, Hollaender and Claus⁸³ have given data on the energy required for the inactivation of *Es. coli* as a function of the wave-lengths employed. At 2250A, the ergs required per bacterium were 41.3×10^{-6} ; at 2650A, 13.1×10^{-6} ; and at 2950A, 81.6×10^{-6} . These values were regarded as somewhat more accurate than those cited in preceding paragraphs since they were calculated by a method which corrected for the protective action of nonviable organisms.

Lehner⁸⁴ states that although *Rhodovibrio* is killed quickly by ultraviolet rays, *Thiocystis* is not killed by an exposure of an hour, and that short exposures accelerate growth.

ACTION OF ULTRAVIOLET RAYS ON YEAST

Lacasagne⁸⁵ exposed *Saccharomyces ellipsoideus* to radiations of wave-lengths between 2800 and 3800A and found the cells to fall into three classes according to their susceptibility to the rays. Some died immediately, some after a certain period and others exhibited only a retarded rate of cell division but ultimately recovered their power of reproduction. Wyckoff and Luyet⁸⁶ made similar observations and noted the production of some giant cells. Their results tended to indicate "multiple-quantum-hit" relations.

In the work of Oster⁸⁷ carefully prepared suspensions of *Saccharomyces cerevisiae* containing practically no clumps of cells were employed. Following irradiation, observation with a microscope revealed certain abnormalities in cell growth and reproduction. There was apparent a period of survival during which normal colonies could not be formed, after irradiation by each of the wave-lengths (2225 to 3132A) studied. There could be distinguished single cells of normal size and not visibly altered, single cells of giant size, two-cell groups usually from three to eight times the size of normal two-cell groups and more spherical in shape and often showing a long filament-like process constricted at intervals along the length, three to eight-cell groups of giants, which at this stage either cease budding or go on to furnish buds of normal size, and finally larger groups which, although retarded in their ability to form normal-sized colonies show little evidence of giantism. At all wave-lengths, a definite, measurable retardation in reproduction as based upon the criterion of culture formation could be demonstrated. The size of the colonies increased at a rate roughly proportional to the increase in incident energy. The relation between the percentage of inhibition and the incident energy appeared to be logarithmic over the inhibitory range. When the period of exposure was increased beyond this point, various degrees of injury occurred and finally all budding and growth could be stopped. As a criterion of lethal action, Oster adopted the inability of the yeast cell to form two or more daughter cells rather than merely the inhibition of macroscopic colonies. The survival-ratio is then the ratio of the number of cells which bud at least twice to the original number of exposed cells. For each of several wave-lengths shorter than 2900A curves were plotted of the survival-ratio against the energy in ergs per sq. mm. In the case of longer wave-lengths very much more incident energy was required for lethal effects.

The curves revealed that for all wave-lengths studied the energy which had to be applied before any of the cells were killed was approximately 8 per cent of that required

⁸³ Hollaender, A., and Claus, W. D., *J. Gen. Physiol.*, **19**, 753 (1936).

⁸⁴ Lehner, A., *Zentr. Bakt., Parasitenk.*, (Abt. II), **97**, 65 (1937); *Chem. Abs.*, **32**, 1743 (1938).

⁸⁵ Lacasagne, A., *Compt. rend.*, **190**, 524 (1930).

⁸⁶ Wyckoff, W. R. G., and Luyet, B. J., *Radiology*, **17**, 1171 (1931).

⁸⁷ Oster, R. H., *J. Gen. Physiol.*, **18**, 71 (1934-5).

to kill all the cells. Between 20 and 30 per cent of the cells do not survive after an exposure relatively short in comparison with that required to suppress budding in all of the cells. The remaining 70 or 80 per cent require from 70 to 80 per cent of the energy required to kill all the cells. The last 2 or 3 per cent of the cells are affected at a slightly lower rate. Cells irradiated with small amounts of energy show a much lower rate of budding with a longer initial lag period than that of the typical growth curve of normal cells. The age of the cells has a marked influence upon their resistance, from 20 to 50 per cent more energy being required to produce a given effect on a fifteen-day culture than on 24-hour cultures. In the former, a greater proportion of the cells is in the resting stage.⁸⁸

The temperature coefficient is low, about 1.06 to 1.1, in agreement with that obtained by Gates on bacteria. The irradiation effects are exerted directly upon the organisms since irradiation of the malt-agar medium for periods from five minutes to two hours had no effect upon the growth of organisms subsequently planted in it. For intensity variations up to 30 per cent, the rate of absorption of photons by the cells did not markedly affect the lethal action.

Attempts to determine the absorption spectrum of yeast failed to give satisfactory results. However, an application of the method of Gates of plotting the reciprocals of the energies required to cause death in 50 per cent of the cells against the wave-lengths employed, gave results similar to those reported by Gates for bacteria. The necessary energies ranged from 457 ergs per sq. mm. at 2652Å to 23,500 ergs at 3022Å, or roughly five times the energy range for *Staphylococcus aureus*.

From the individual survival-ratio curves plotted against the incident energies applied, Oster calculated (by a method devised by Curie,⁸⁹ which differs somewhat from that employed by Wyckoff), the number of quantum-hits necessary to kill at various wave-lengths. The results indicated a "multiple-quantum hit-to-kill" relation, the minimum number of quantum hits varying from about four to about six. The shape of the curves was believed to suggest that other factors than single quantum hits on several molecules are involved, as suggested by Rahn, or multiple-quantum hits on a sensitive volume element, as suggested by Wyckoff and Luyet.

Stimulation of Yeast There have been many attempts to show the stimulation of yeast growth by irradiation by ultraviolet light. Some authors believed that wave-lengths somewhat longer than the lethal ones have such an action. Loofbourow and Cameron, who reviewed the literature,⁹⁰ were themselves unable to detect such an action, and this is the generally accepted conclusion.

There have, however, been suggestions that sublethal doses of radiation in the lethal wave-length range may produce injuries of the cells by virtue of which products capable of stimulating the growth of other cells are formed. Hollaender and Duggar⁹¹ observed that cells from the 10 per cent which survived a certain irradiation in isotonic salt suspension by the 2650Å rays increased in number when transferred to salt solutions (single or balanced) in which normal control cells died. Fardon, Norris, Loofbourow and Ruddy⁹² claimed that substances which stimulate the respiration of other cells are produced in cells injured by ultraviolet light. Subsequently, these observers⁹³ devised a method for demonstrating the formation of growth-stimulating substances in the injured cells. The active substances were allowed to diffuse from the injured cells through an agar gel upon

⁸⁸ For comparison with the effects of x-rays at various stages of the reproductive period, see Lacasagne, A., and Holweck, F., *Compt. rend. soc. biol.*, 104, 1221 (1930); *Compt. rend.*, 190, 524, 527 (1930); *Compt. rend. soc. biol.*, 103, 60 (1930); Strangeways, T. S. P., and Hopwood, F. L., *Proc. Roy. Soc.*, 100B, 283 (1926); Holweck, F., *Congress Intern. Elec., Paris*, 10, 1 (1932).

⁸⁹ Curie, M., *Compt. rend.*, 188, 202 (1929).

⁹⁰ Loofbourow, J. R., and Cameron, J., *Bull. Basic Sci. Research*, 5, 33 (1933).

⁹¹ Hollaender, A., and Duggar, B. M., *J. Bact.*, 33, 16 (1937).

⁹² Fardon, J., Norris, R. J., Loofbourow, J. R., and Ruddy, M., *Nature*, 139, 589 (1937); Fardon, J. C., Carroll, M. J., and Veronita, M., *Studies Inst. Divi Thomae*, 1, 17, 41 (1937).

⁹³ Sperti, G., Loofbourow, J. R., and Dwyer, C. M., *Studies Inst. Divi Thomae*, 1, 162 (1937).

the surface of which a fresh colony was placed. Colonies grew more rapidly on agar above injured cells than on agar above normal cells.

In earlier experiments, Pulkki⁹⁴ had been unable to produce a stimulant for *B. mycoides* by irradiation of yeast cells. Abderhalden⁹⁵ was unable to alter significantly the course of alcoholic fermentation due to yeast cells by the addition of alcoholic extracts of irradiated yeast, irradiated yeast macerated juice, or ergosterol. Woodrow, Bailey and Fulmer⁹⁶ believed irradiation of yeast culture media produces a non-volatile toxic material derived from the sugar present, but Oster was unable to detect any toxic substance liberated by the organism during its irradiation.

Suranyi and Vermes⁹⁷ claimed to have observed an increase of about 50 per cent in the oxygen consumption of yeast at pH 7.2 during irradiation. Oster, however, could detect no observable effects on oxygen consumption until more than 80 per cent of the organisms had been so affected that normal colonies did not result from their subsequent growth.

Teindl-Czech⁹⁸ found visible light to have no influence on the division rhythm of yeast cells. The same was true for very small exposures from an unfiltered Uviol lamp. Immediately after medium doses the number of cell divisions decreased: this was followed by a temporary rise and a new decrease. During irradiation the yeast appeared slightly vitreous and turbid. With strong doses, abnormal cell forms appeared. Irradiation by the region between 2300 and 4000A in the absence of oxygen may be used to secure yeast cells of uniform potency.⁹⁹

Fermentation. Zeller¹⁰⁰ found sunlight to inhibit the output of carbon dioxide from yeast after a temporary slight stimulation. Guerrini¹⁰¹ inoculated yeast into 5-per cent glucose solutions and incubated the cultures in darkness, in daylight and in light filtered through red, green, yellow and blue screens. He claimed to find the liberation of carbon dioxide to be greater in cultures exposed to light than in those in darkness. In general, the greatest quantities of carbon dioxide were produced in red light, the next greatest in yellow, then in green and the least in blue light. The last gave practically no carbon dioxide. Murakami¹⁰² found that in the fermentation of koji extract the production of alcohol was maximal under a red light of wave-length longer than 6200A, increasing in general with the wave-length. The maximum yield of aldehyde was obtained under wave-lengths between 3960 and 5400A. Acetal was produced abundantly under a white light. The production of volatile acid was greatest in darkness and that of non-volatile acid greatest in violet to yellow light. The production of esters was generally higher under light of longer wave-lengths. There have been a number of claims that ultraviolet light increases the fermentative power of yeast.

Lindner¹⁰³ found that under normal conditions 30 gms. of dextrose gave 119 cc. of carbon dioxide in 24 hours and under ultraviolet irradiation 2743 cc. In the same

⁹⁴ Pulkki, L. H., *Ann. Acad. Sci. Fennicae*, **A41**, No. 1 (1935); *Chem. Abs.*, **30**, 4898 (1936).

⁹⁵ Abderhalden, E., *Fermentforsch.*, **9**, 195 (1927); *Brit. Chem. Abs.*, **A**, 1113 (1927).

⁹⁶ Woodrow, J. W., Bailey, A. C., and Fulmer, E. I., *Plant Physiol.*, **2**, 71 (1927).

⁹⁷ Suranyi, G., and Vermes, M., *Magyar Orvosi Arch.*, **30**, 585 (1929); *Chem. Abs.*, **25**, 2162 (1931).

⁹⁸ Teindl-Czech, L., *Protoplasma*, **27**, 313 (1937). Note also Palmieri, G. G., and Giordano, G., *Boll. soc. ital. biol. sper.*, **7**, 1318 (1932); *Chem. Abs.*, **27**, 1371 (1933).

⁹⁹ Light, R. F., Frey, C. N., and Patitz, G. J., U. S. P. 2,099,025, Nov. 16, 1937; *Chem. Abs.*, **32**, 300 (1938).

¹⁰⁰ Zeller, H., *Biochem. Z.*, **171**, 45 (1926).

¹⁰¹ Guerrini, G., *Boll. soc. ital. biol. sper.*, **5**, 635, 1098 (1930); *Chem. Abs.*, **25**, 534 (1931).

¹⁰² Murakami, R., *J. Agr. Chem. Soc. Japan*, **8**, 1237 (1932); **9**, 672 (1933); *Chem. Abs.*, **27**, 1983, 5470 (1933); *Bull. Utsunomiya Agr. Coll.*, **3**, 29 (1933); *Chem. Abs.*, **28**, 3519 (1934).

¹⁰³ Lindner, P., *Woch. Brau.*, **39**, 166 (1922); *Chem. Abs.*, **17**, 1686 (1923).

period.¹⁰⁶ De Fazi¹⁰⁶ claimed to have observed a stimulation of growth and fermentation of yeast. His investigations involved in some cases irradiation of the water used in dissolving the sugar to be fermented rather than of the yeast or fermenting mixture. Even under the former conditions, some stimulation was stated to occur. Also, such claims have been made by Sanzo and Pirrone.¹⁰⁷

Owen and Mobley¹⁰⁷ have reported that exposure of yeast to ultraviolet light increases its growth and its fermenting power. An exposure of one minute to radiations of wavelengths 2300 to 3100Å gave the greatest stimulation, but an exposure of three minutes had the opposite effect. Since a similar stimulation could be brought about, they believed, by the irradiation of sterilized molasses wort, they did not attribute the stimulation to the death of harmful contaminating microorganisms. Beckwith and Donovan¹⁰⁸ exposed a 36-hour culture of purified brewers' yeast in a layer 1.15 cm. thick to ultraviolet radiations for 1.4 seconds per cc. Of the irradiated culture, 125 cc. were added to 1600 cc. of sterilized beer wort and incubated at 28°C. for 32 days. Alcohol formation was at first depressed, but from the 9th to 32nd days exceeded that in the control. Irradiation of the wort alone was without effect. Marmeli and Baratto¹⁰⁹ find that fermentation may be accelerated by addition of small quantities of such substances as ascorbic acid, β -carotene, acamnine, adenine, phytin or inosine. The effects were claimed to be enhanced by previous irradiation of these substances.

Tanner¹¹⁰ found ultraviolet light to have only a depressing action on fermentation, whether the yeast, the fermenting culture or the glucose broth was the subject of the irradiation. According to Reynolds and Wynd,¹¹¹ the inhibition of fermentation by radiations between 3000 and 2500Å is a specific effect independent of general injury to the cells. Von Euler and Swartz¹¹² believed the efficacy of ultraviolet light in accelerating the synthesis of organic phosphoric esters during fermentation to be doubtful, although the inorganic phosphate is decreased.

According to Keeser,¹¹³ glucolysis of 0.1-per cent glucose solution in the presence of yeast cells was accelerated by irradiation with red light for thirty minutes, but white, green or blue light had little effect. Similar results were obtained with fructose, and also in the glucolysis of glucose or fructose by guinea pig serum. Irradiation of ox serum for five hours did not alter the reducing power or content of inorganic phosphorus of the serum, but ultraviolet irradiation increased the reducing power without altering the inorganic phosphorus.

The effect of carbon monoxide in inhibiting the anaerobic fermentation of tetanus or gas gangrene bacilli is increased by light, according to Schlayer.¹¹⁴ Since only the combination of carbon monoxide with an iron compound is dissociated by light, the fermentation enzyme of these organisms must be an iron catalyst. In the case of an anaerobic butyric acid fermentation process, Kempner and Kubowitz¹¹⁵ could demonstrate a similar phenomenon only at low temperatures and by the use of very great light intensities. Under these conditions, the fermentation can be completely and reversibly inhibited by carbon monoxide, light destroying the

¹⁰⁶ See also Söbngen, N. L., and Coolhaas, C., *Woch. Brau.*, 40, 187 (1923); *Chem. Abs.*, 18, 1030 (1924); Rennhard, A. W., *Compt. rend. soc. biol.*, 89, 1080 (1923).

¹⁰⁷ De Fazi, R., *Ann. Chim. Applicata*, 4, 301 (1915); 6, 221 (1916); 8, 93 (1917); *Chem. Abs.*, 10, 950 (1916); *J. Ind. Eng. Chem.*, 13, 265 (1921); *Atti R. Accad. Lincei*, 5, 344, 901 (1927); *Brit. Chem. Abs.*, A, 592, 1113 (1927); *Chem. Abs.*, 21, 2045 (1927).

¹⁰⁸ Sanzo, L., and Pirrone, F., *Atti Accad. Lincei*, 13, 613 (1931); *Chem. Abs.*, 26, 2990 (1932).

¹⁰⁹ Owen, W. L., and Mobley, R. L., *Zentr. Bakt. Parasitenk., Abt. II*, 83, 273 (1933); *Chem. Abs.*, 27, 5470 (1933); Owen, W. L., *Food Ind.*, 5, 252 (1933); *Chem. Abs.*, 28, 254 (1934).

¹¹⁰ Beckwith, T. D., and Donovan, S. E., *Proc. Soc. Exptl. Biol. Med.*, 35, 36 (1936).

¹¹¹ Marmeli, E., and Baratto, A., *Ann. chim. farm.*, No. 1, 18 (1938); *Chem. Abs.*, 32, 6269 (1938).

¹¹² Tanner, F. W., *J. Ind. Eng. Chem.*, 13, 265 (1921); *Chem. Gaz.*, 75, 309 (1923); Tanner, F. W., and Byerley, J. R., *Arch. Microbiol.*, 5, 349 (1934); *Chem. Abs.*, 28, 5594 (1934).

¹¹³ Reynolds, E. S., and Wynd, F. L., *Ann. Mo. Bot. Gardens*, 22, 853 (1935); *Chem. Abs.*, 30, 3855 (1936).

¹¹⁴ von Euler, H., and Swartz, O., *Arkiv Kemi, Mineral. Geol.*, 9, 21 (1925).

¹¹⁵ Keeser, E., *Arch. Exptl. Path. Pharmacol.*, 170, 500 (1933).

¹¹⁶ Schlayer, C., *Biochem. Z.*, 276, 460 (1935).

¹¹⁷ Kempner, W., and Kubowitz, F., *Biochem. Z.*, 265, 245 (1933).

inhibition. The light-sensitivity is very much smaller than in the case of the carbon monoxide combination with the enzyme concerned with respiration. The carbon monoxide compound of the enzyme concerned in the butyric acid fermentation absorbs within the special range 6500 to 3660 Å.

The action of photocatalysts in the fermentation of lactose by *Es. coli* is stimulating or inhibiting according to the quantity and quality of the catalyst.¹¹⁶

Molds. Reports on molds are conflicting. Some workers state that molds are killed by exposure to ultraviolet light without much difficulty.¹¹⁷ Others report that molds are killed by ordinary exposure only when present in very small amounts. Some molds have protection in the form of fatty or waxy secretions. The latter may shield the mold from some radiations.

Fulton and Coblenz¹¹⁸ exposed spores of 27 species of fungi for one minute to ultraviolet radiation from a mercury tungsten arc at a distance of six inches. There was complete killing of the spores of 16 species and a survival of less than 1 per cent in four species. It was hoped that this process could be applied to the killing of molds and fungi on oranges. Such a dosage caused no injury to the fruit. The limitation of the method, however, lies in the fact that the rays do not penetrate sufficiently beneath the surface to afford complete disinfection of the fruit.

Dillon-Weston¹¹⁹ finds the spores of *Puccinia graminis tritici* to be killed more easily when irradiated in water than when irradiated dry. The white and orange specimens of certain physiological forms of the fungus are more susceptible than the red and gray ones. The pigments of the spore walls probably have some protective action. Sibilia¹²⁰ believed that ultraviolet rays activate the germination of the teleutospores of *Puccinia coronifera* of oats and *P. triticea* and to a lesser extent of *P. graminis*.

Smith¹²¹ finds the death of *Fusarium* spores exposed to ultraviolet light at different temperatures to take the form of sigmoid curves which rapidly approach the logarithmic type as the temperature is increased. The average temperature coefficient between 0 and 40°C. is 1.13, but between 40 and 50°C. it is 1.37.

Johnson¹²² finds rays in the Schumann region to be highly destructive to the upper layers of the mycelium of the fungi, *Collybia dryophila*, *Sclerotium bataticola*, and *Fusarium batatia*. The effect was localized and did not extend deeply into the culture. Ultraviolet rays passing through Vitaglass had a more injurious effect than those passing the Corning filter 980A. Those passing through Cellophane were intermediate in their action. According to Ramsey and Bailey,¹²³ irradiation by a quartz mercury arc stimulates spore formation in cultures of *Macrosporium tomato* and *Fusarium cepae*.¹²⁴

Viruses and Bacteriophages. According to Baker and Nanavutty,¹²⁵ the bacteriophages are about as susceptible as the bacteria to irradiation, and the rela-

¹¹⁶ Guerrini, G., *Boll. soc. ital. biol. sper.*, 10, 847 (1935); *Chem. Abs.*, 30, 8284 (1936).

¹¹⁷ Houghton, E. M., and Davis, L., *Am. J. Public Health*, 4, 224 (1914); Fairhall, L. T., and Bates, F. M., *The Cotton Oil Press*, 33 (1921).

¹¹⁸ Fulton, H. R., and Coblenz, W. W., *J. Agr. Research*, 38, 159 (1929).

¹¹⁹ Dillon-Weston, W. A. R., *Sci. Agr.*, 12, 81 (1931); *Chem. Abs.*, 26, 497 (1932); Dillon-Weston, W. A. R., and Hainan, E. T., *Phytopathology*, 20, 959 (1930); *Chem. Abs.*, 25, 2233 (1931).

¹²⁰ Sibilia, C., *Boll. staz. patol. vegetale*, 11, 115 (1931); *Chem. Abs.*, 26, 1958 (1932).

¹²¹ Smith, E., *Bull. Torrey Bot. Club*, 62, 45 (1935); *Chem. Abs.*, 29, 1130 (1935).

¹²² Johnson, F. H., *Phytopathology*, 22, 277 (1932).

¹²³ Ramsey, G. B., and Bailey, A. A., *Bot. Gaz.*, 89, 113 (1930); *Chem. Abs.*, 24, 3261 (1930).

¹²⁴ See Hutchinson, A. H., and Ashton, M. R., [*Canadian J. Research*, 3, 187 (1930); *Chem. Abs.*, 25, 315 (1931)] for the action of various mercury lines on the fungus, *Colletotrichum phomoides*.

¹²⁵ Baker, S. L., and Nanavutty, S. H., *Brit. J. Exp. Path.*, 10, 45 (1929); see also Appelmann, R., *Arch. Intern. Pharmacodyn.*, 21, 95 (1922); *Chem. Abs.*, 17, 1978 (1923).

tive efficiencies of various spectral regions are about the same as for *B. coli*. Mizuno¹²⁶ found the destructive action to vary with the medium, being weak in broth, moderate in water and strongest on agar plates. Among the bacteriophages which have been affected by irradiation are those for *B. coli* D,¹²⁷ cholera, staphylococci, and dysentery.¹²⁸ The ultraviolet absorption of colon bacteriophages has been measured by Sandholzer, Mann and Berry.¹²⁹

The work of Rivers and Gates¹³⁰ indicates that the susceptibility of vaccinia virus to irradiation is of the same order as that of bacteria. Galloway¹³¹ finds the virus of foot-and-mouth disease to be destroyed after five minutes of exposure of filtrates to the radiations of a quartz mercury arc in quartz vessels. Also, the virus is inactivated after thirty minutes if the rays are filtered through Vitaglass. In ordinary glass there is no lethal action.

The tobacco mosaic disease virus is similarly inactivated,¹³² unless it has penetrated plant tissue. Stanley¹³³ finds 0.5-per cent solutions of the crystallized protein of this virus to produce (when irradiated for eight hours by the unfiltered rays of a quartz mercury arc) an inactive protein which retains certain chemical and serological properties of the original. However, the protein no longer is capable of producing either the mosaic disease or a high molecular weight protein on inoculation into Turkish tobacco plants. Neither does it cause local lesions in *Nicotinea glutinosa*. The product may be crystallized from solution but the crystal is more opalescent and more readily denatured than before irradiation. Its x-ray diffraction pattern, isoelectric point and optical rotation are unchanged. No marked change in molecular weight occurs, although the homogeneity of the molecules is decreased. The serum of an animal previously injected with the irradiated product has a neutralizing effect on the original virus. The survival-ratios during irradiation follow a simple exponential curve, the rate of the inactivation depending upon the incident energy, according to Price and Gowen.¹³⁴ The absorption spectrum of the crystalline virus differs from that of other proteins in having its absorption maximum at 2650 Å.¹³⁵ This suggests that the compound is a nucleoprotein, and for this there is independent chemical evidence. This suggestion is interesting in that it points to the conclusion that viruses, which lie on the border between the living and the lifeless, appear to have nucleic acid as a component.

Other viruses found to be inactivated by ultraviolet rays include those of herpes and encephalitis,¹³⁶ influenza,¹³⁷ and crystalline tomato bushy stunt virus.¹³⁸

It has been shown by Herzberg¹³⁹ that certain dyes can sensitize the vaccine virus to visible light. Only the thiazine, acridine and thioxanthone dyes were stated to have this property. At a dilution of one in a million, methylene blue and thiopyronin acted the most rapidly, sensitizing the virus within twenty to forty seconds. For exposures of an hour the acridine dyes were found to be

¹²⁶ Mizuno, K., *Japan J. Med. Sci., Bact. & Parasit.*, **1**, 52 (1929); *Chem. Abs.*, **23**, 5485 (1929).

¹²⁷ McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 408 (1926).

¹²⁸ Levaditi, C., and Voet, J., *Compt. rend. soc. biol.*, **120**, 385 (1935); *Chem. Abs.*, **30**, 1084 (1936); see also Hallauer, C., *Z. Infektionskrankh.*, **117**, 18 (1935).

¹²⁹ Sandholzer, L. A., Mann, M., and Berry, G. P., *J. Bact.*, **33**, 17 (1937).

¹³⁰ Rivers, T. M., and Gates, F. L., *J. Exp. Med.*, **47**, 45 (1928).

¹³¹ Galloway, I. A., *Brit. J. Exptl. Path.*, **9**, 326 (1928).

¹³² Arthur, J. M., and Newell, J. M., *Am. J. Bot.*, **16**, 338 (1929); **15**, 623 (1928).

¹³³ Stanley, W. M., *Science*, **83**, 626 (1936).

¹³⁴ Price, W. C., and Gowen, J. W., *Phytopathology*, **27**, 267 (1937).

¹³⁵ Lavin, G. I., and Stanley, W. M., *J. Biol. Chem.*, **118**, 269 (1937).

¹³⁶ McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 408 (1926).

¹³⁷ Wells, W. F., and Brown, H. W., *Am. J. Hyg.*, **24**, 407 (1936).

¹³⁸ Bawden, F. C., and Pirie, N. W., *Brit. J. Exptl. Path.*, **19**, 251 (1938).

¹³⁹ Herzberg, K., *Z. Immunitäts*, **80**, 507 (1933); *Chem. Abs.*, **28**, 5126 (1934).

effective in the greatest dilutions, one in fifty million. It was pointed out that irradiation of rabbit skin by short wave-lengths after the application of active virus (within eight hours of the inoculation) reduced the number of pustules produced, but no effects could be observed if the irradiation was given after sixteen hours. After the injection of methylene blue intravenously, irradiation modified the infection even when given 24 hours after inoculation. With light of longer wave-lengths, no modification could be produced by irradiations made later than seven hours after the inoculation, even in the presence of the dye. The same effect was obtained with sunlight used 24 hours after inoculation as with the best source of ultraviolet light used 72 hours after inoculation.

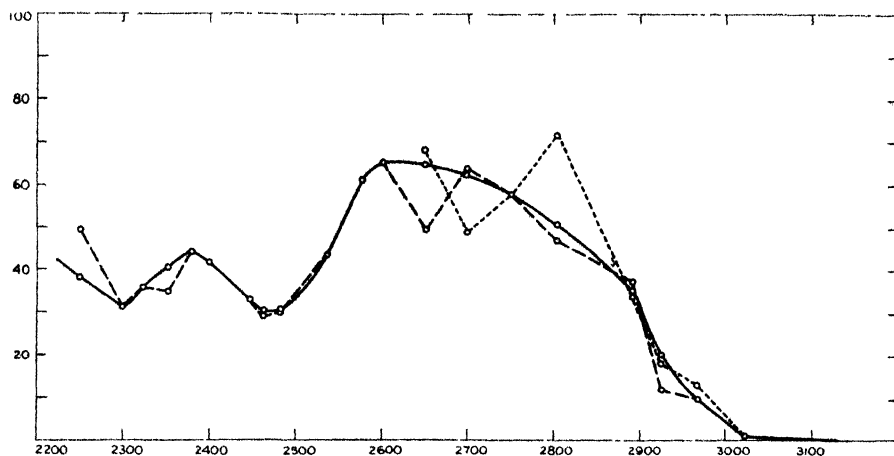


FIGURE 136. Radiotoxic Spectral Sensitivity of *Chlorella vulgaris* to Ultraviolet Rays. (From Meier, Smithsonian Miscellaneous Collections. The abscissae are wave-lengths in Angstroms. The ordinates are relative lethal effectiveness in arbitrary units. Black line, smooth curve; dash line, actual values; dotted line, curve obtained by Meier, 1934).

Algae. Lami¹⁴⁰ found that ultraviolet irradiation of the alga, *Bonnemasonia asperagoides*, causes liberation of iodine from the gland cells. In the case of *Euglena*, Swann and del Rosario¹⁴¹ found that in killing by α -particles, death was caused by a single impact with some sensitive entity of the cell, the size of which was about equal to that of the nucleus. In experiments with ultraviolet light, it appeared that the cells did not cease to die the moment irradiation was stopped, some cells apparently being affected in a manner which produced death some time later. Attempts were made to utilize absorption data on different parts of the cell to compute the volume of an assumed sensitive entity, on the assumption that the probability of reaction following absorption of a photon is unity. Attempts were also made to calculate the probability of killing on the basis that the volume of the assumed sensitive entity is that of the nucleus.

Meier¹⁴² reported that the unicellular green alga, *Chlorella vulgaris*, is not killed by wave-lengths longer than 3022Å. In subsequent work,¹⁴³ she irradiated

¹⁴⁰ Lami, R., *Compt. rend.*, 191, 863 (1930).

¹⁴¹ Swann, W. F. G., and del Rosario, C., *J. Franklin Inst.*, 213, 549 (1932).

¹⁴² Meier, F., *Smithsonian Misc. Coll.*, 87, No. 10 (1932).

¹⁴³ Meier, F., *Ibid.*, 92, No. 3 (1934); 95, No. 2 (1936).

agar plates and inoculated them. As normal growth resulted, she concluded that radiations lethal to the organisms did not affect the medium in any way to accelerate or retard growth. She then made a number of exposures of plates (inoculated two to five months previously) behind a spectrograph for various periods from a few seconds to several hours and noted the regions in which decolorized areas became evident at intervals of from a few days to two months following irradiation. The lethal radiotoxic threshold for wave-lengths 2652 and 2804A lies between 100 and 120 seconds for intensities of 1960 and 1840 ergs per sq. cm. per second, respectively. Assuming the Bunsen-Roscoe law, for 1000 ergs per sq. cm. per second, the exposures required for 2652A would be 220 seconds and for 2804A, 206 seconds. Similarly, the results at a number of other wave-lengths

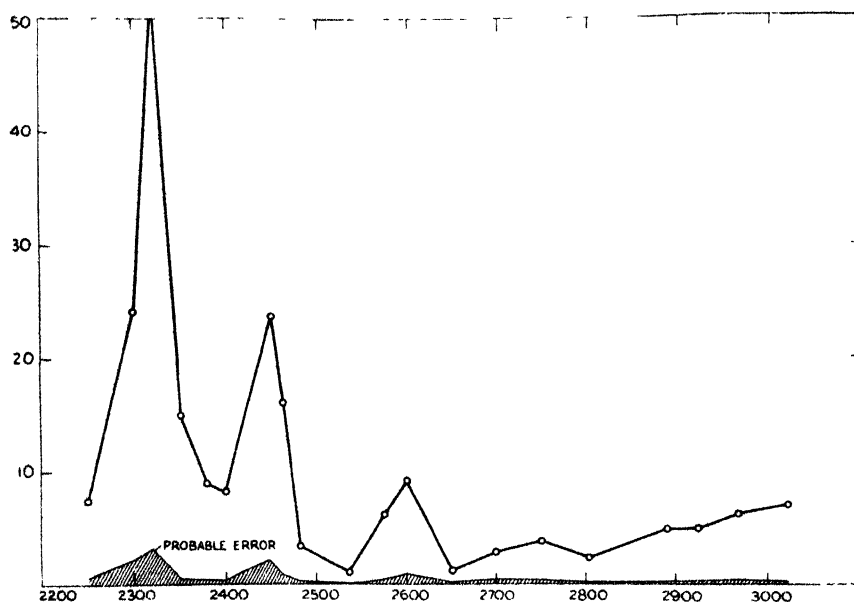


FIGURE 137. Radiotoxic Virulence Determined from *Chlorella vulgaris*. (From Meier, Smithsonian Miscellaneous Collections). The abscissae are wave-lengths in Angstroms. The ordinates are radiotoxic virulence in arbitrary units.

were reduced to this common intensity and plotted in Figure 136 which shows a maximum lethal sensitivity at about 2600A. (Note similarity to the observations of Gates on bacteria.)¹⁴⁴ At the suggestion of Dr. C. G. Abbot, she introduced two new terms, radiotoxic spectral sensitivity and radiotoxic virulence. The former related to the certainty of the lethal action and the latter to the quickness of the attack. The distinction was drawn because death ensued much more quickly after irradiation in some spectral regions than in others. The data on the radiotoxic virulence are included in Figure 137 and show an alternate waxing and waning with decreasing wave-length and a high maximum at 2323A.¹⁴⁵

¹⁴⁴ Note also Duggar, B. M., and Hollaender, A., *J. Bact.*, **27**, 219 (1934), Lucas, F., *Bell System Tech. Publ. Metallurgy Monogr.*, **B 792**, 1-47.

¹⁴⁵ For effects of portions of the visible and ultraviolet spectrum on cells of the prothallium of ferns, see Charlton, F. B., *Am. J. Botany*, **25**, 431 (1938).

Higher Plants. Hertel examined leaves of the aquatic plant *Elodea canadensis* under a microscope with a quartz condenser and illuminated with light of 2800Å. The streaming movement of the granules in the living cells ceased almost immediately.

Work relating to the lethal effects of ultraviolet light on plant cells has been reviewed by Delf.¹⁴⁶ That single exposures may produce severe reactions was demonstrated by Maquenne and Demoussy in 1909, Kluyver in 1911, Ursprung and Blum in 1917, and Stoklasa in 1911. In Kluyver's experiment, exposures at 40 cm. from a mercury-vapor lamp for two and a half hours showed no immediate effects on leaves of *Aucubus*. Subsequently, however, the epidermal cells died, turning black in all leaves which had been exposed for forty minutes or longer. A cover glass protected a leaf from lethal effects over an exposure of twenty hours, indicating that rays of 3000Å or longer do not have a directly harmful effect on the plant. The red pigment of *Begonia* was destroyed by illumination for two and a half hours.

According to Ursprung and Blum, in *Pelargonium* the white parts are more resistant to ultraviolet than the green ones in the variegated leaf but in *Vicia faba* the opposite seems to be true. In general, it seems that the guard cells of the stomata are the most resistant of all the epidermal cells. The epidermis, and especially the cuticle, appear to absorb ultraviolet light, the cells being destroyed by the irradiation although the tissues below appear unharmed. Russell and Russell showed that cress seedlings grown on muslin were stunted by mercury-arc irradiation and that those irradiated for periods as long as twenty minutes daily were shriveled in appearance.¹⁴⁷

Delf, Ritson and Westbrook¹⁴⁸ tested the effects of very short daily exposures to the mercury arc upon a variety of plants. In general, they noted delayed germination, retarded growth and stunted habit of the seedlings and a partial inhibition of leaf development, especially of the lamina. In some cases there was a darker green color and in one case a loss of anthocyanin pigment in the lamina. With longer exposures, older plants showed a promoted leaf fall, and retardation of flower formation and of the opening of previously formed buds. In these cases the exposures were from two to ten minutes repeated from four to eight times daily. With exposures of thirty seconds or less the results were different. In one case, flowering of *Pelargonium* seemed to be promoted, in another the leaves of the irradiated plant ultimately surpassed those of the control in size; and in a third case, after a month of thirty-second daily irradiations at a distance of eight feet, there was a permanent and very favorable after effect in *Trifolium*. In the plant *Voandzeia*, exposures of five minutes daily led to definite anatomical changes during development, such as a reduction in the total thickness of lamina, development of more compact mesophyll with smaller and fewer air spaces, reduction in mechanical tissue and collapse of the cells of the upper epidermis followed by the withdrawal of the chloroplasts from the upper parts of the palisade cells. Martin and Westbrook¹⁴⁹ made histological examinations of leaves (*Pulmonaria* or *Aucuba*) at varying periods during irradiation. Lethal changes were first evident in the epidermal cells in the nuclei which coagulate, darken and become disorganized to one or more irregular masses. Later the cytoplasm becomes finely granular

¹⁴⁶ Delf, E. M., *Brit. J. Actinotherap.*, 2, 106 (1927).

¹⁴⁷ Kluyver, A. J., *Sitzb. Math. Acad. Wiss., Wien.*, 120, 195 (1911); *Chem. Abs.*, 6, 3108 (1912); Ursprung, A., and Blum, G., *Ber. Deut. Bot. Ges.*, 35, 385 (1917); Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1925.

¹⁴⁸ Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, 5, 138 (1927).

¹⁴⁹ Martin, B. T., and Westbrook, M. A., *J. Exptl. Biol.*, 7, 293 (1930).

and rapidly darkens. For small doses the reciprocal of the latent period for visible browning is proportional to the dose expressed in Clark lithopone units, but doses between ten and fifteen units make the latent period very short. During irradiation the temperature coefficient was about 1.1, but during the latent period it was higher, from 1.32 to 2.9.

Gilles,¹⁵⁰ states that the germination of lentil and turnip seeds is accelerated but their growth is somewhat retarded by mercury-arc irradiation.

Protozoa. There have been comparatively few investigations of the effects of ultraviolet light on amoebae.¹⁵¹ Heilbrunn and Daugherty assumed that ultraviolet rays cause first a breakdown of a calcium gel in the cortex followed by the entry of this calcium into the interior where it produces a preliminary liquefaction followed by gelation. According to Black¹⁵² media which favor motility tend to exert a synergistic action with the rays (2540Å) in decreasing motility and producing cytolysis.

Paramecia have been studied under radiations. Hughes and Bovie¹⁵³ observed cytolysis in this organism under ultraviolet irradiation. Harris and Hoyt¹⁵⁴ employed paramecia in their work on the significance of the aromatic amino-acids to which allusion has been made. Bovie and Daland¹⁵⁵ found the short rays in the fluorite region to render *Paramecium caudatum* so sensitive to heat that amounts of heat insufficient to affect non-irradiated cells become lethal. Longer exposures to these rays caused death directly.¹⁵⁶ Bills¹⁵⁷ found that sunlight, but not indirect daylight, inactivates these organisms.

Weinstein¹⁵⁸ has given a curve (see Figure 134) for the relation between the wave-lengths used and the lethal action. It differs considerably from the analogous curves for bacteria in that the longer wave-lengths show greater effectiveness. In the case of such large cells there is some evidence to show that an optimum lethal action may occur closer to 2800Å, the position of the maximum absorption by proteins, than to 2600Å, that of the maximum absorption by nucleic acids. Leighton and Giese¹⁵⁹ have criticized the long wave-length limit indicated in the curve of Weinstein. They found that, although doses of only 16,500 ergs per sq. mm. sufficed to kill paramecia at 3025Å within 24 hours after the irradiation, far greater dosages of the wave-length 3130Å were ineffective. Doses as high as 191,000 to 200,000 ergs per sq. mm. had little if any effect. Weinstein had reported that the organism is killed about one-ninth as readily at 3130Å as at 2654Å and one-half as readily as at 3025Å. Leighton and Giese attribute Weinstein's results to the presence of stray radiations, possibly the result of scattering within the quartz prism, in the light assumed to be of the wave length 3130Å. In general, Leighton and Giese found that to produce vesiculation (their criterion of death) in 50 per cent of the cells, a large number of quanta, 10^{13} , must be absorbed by each paramecium.

Hutchinson and Ashton¹⁶⁰ employed monochromatic light (both visible and

¹⁵⁰ Gilles, E., *Compt. rend. soc. biol.*, **109**, 739 (1932); *Chem. Abs.*, **27**, 3969 (1933).

¹⁵¹ Folger, H. T., *J. Exp. Zool.*, **51**, 261 (1925); Heilbrunn, L. V., and Daugherty, K., *Protoplasma*, **18**, 596 (1933); *Chem. Abs.*, **27**, 4849 (1933).

¹⁵² Black, W. A., *Univ. Calif. Pub. Zool.*, **41**, 75 (1936); *Chem. Abs.*, **30**, 8254 (1936).

¹⁵³ Hughes, D. M., and Bovie, W. T., *J. Med. Research*, **39**, 223, 233 (1918).

¹⁵⁴ Harris, F. I., and Hoyt, H. S., *Science*, **56**, 318 (1917).

¹⁵⁵ Bovie, W. T., and Daland, G. A., *Am. J. Physiol.*, **66**, 55 (1920).

¹⁵⁶ Forbes, H. S., and Daland, G. A., *Am. J. Physiol.*, **66**, 50 (1923).

¹⁵⁷ Bills, C. E., *Biol. Bull. Marine Biol. Lab.*, **47**, 253 (1924).

¹⁵⁸ Weinstein, I., *J. Opt. Soc. Am.*, **20**, 433 (1930).

¹⁵⁹ Leighton, P. A., and Giese, A. C., *J. Gen. Physiol.*, **18**, 557 (1934); *Science*, **81**, 53 (1935).

¹⁶⁰ Hutchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **1**, 292 (1929).

ultraviolet), and in their controls took into account the period of the growth curve at which the specimens were taken. They believed that certain frequencies in the red, yellow and near ultraviolet regions stimulated growth, and the green rays as well as ultraviolet rays shorter than about 3000A retarded growth or killed the cells. Effects were different during the early and later portions of a 24-hour irradiation in some cases.

Alpatov and Nastyukova¹⁶¹ find *Paramecium caudatum* twice as susceptible to the stimulating and depressing actions of radiations as *Paramecium bursaria*, which contains green symbiotic algae. After the latter had been kept in darkness until the algae lost their color, the two species were equally susceptible. The addition of electrolytes which induce swelling in colloids decreased the resistance of the organisms to ultraviolet rays and those which shrink colloids made the organisms more resistant.¹⁶² Increase in viscosity produced by an electric current increased the resistance and decreases in viscosity produced by chloretone decreased resistance to irradiation.

A latent period of several minutes to hours between the cessation of irradiation of *P. bursaria* and the death of many cells has been emphasized by Tang and Gaw,¹⁶³ who have discussed the effects of the age of the organisms upon the constants of an empirical equation for the survival curve.¹⁶⁴ Tchakhotine,¹⁶⁵ by means of an ultramicroscope, observed the flocculation of cell colloids by the passage of a sharp pencil of ultraviolet light into the cytoplasm of amoebae, paramecia, spirogyra and other organisms. Localized flocculations of cytoplasmic proteins cannot be obtained. Nuclear substances change in dispersion but do not precipitate.

Eggs, Embryos, Lower Animal Forms. The oöcysts of *Eimeria tenella*, if unsegmented, suffer a 100 per cent mortality after a ten-minute exposure to a temperature of 53°, 15 seconds at 60° or to three quarters of a zinc sulfide unit of ultraviolet light.¹⁶⁶

Lillie and Baskerville¹⁶⁷ found that exposure of unfertilized eggs of *Arbacia* to ultraviolet light for five to fifteen minutes caused membrane formation and cytolysis. The treated eggs, unless overirradiated, showed the usual increased susceptibility to hypertonic sea water. Even when the radiations had been too weak to produce membranes, the susceptibility to hypertonic sea water was increased. Hinrichs¹⁶⁸ found that regions of high physiological activity were modified first in development by radiations. These regions were also the first to recover from slight injury. Irradiation of the sperm reduced its motility, delayed cleavage and interfered with the normal development of the zygote. Loose sperm suspensions of *Arbacia* lost their fertilizing power more rapidly on irradiation than concentrated ones. The sperm was agglutinated.

Klugh¹⁶⁹ used filters in comparing the effects of various components of sunlight on a series of seven marine organisms which differed widely in their response

¹⁶¹ Alpatov, V. V., and Nastyukova, O. K., *Proc. Soc. Exp. Biol. Med.*, **32**, 99 (1934).

¹⁶² Alpatov, V. V., and Nastyukova, O. K., *Compt. rend. Acad. Sci. U.R.S.S.*, **3**, 595 (1934); *Chem. Abs.*, **29**, 2182 (1935).

¹⁶³ Tang, P. S., and Gaw, H. Z., *Chinese J. Physiol.*, **11**, 305 (1937); *Chem. Abs.*, **31**, 4728 (1937).

¹⁶⁴ Early observations are due to Dreyer, G., *Mitt. Finsens Lichtinstitut*, **4**, 81 (1903); **7**, 98 (1904); Hertel, E., *Z. Allgem. Physiol.*, **5**, 95 (1905); Sonne, C., *Arch. Phys. Therap. X-Ray, Radium*, **10**, 239 (1929).

¹⁶⁵ Tchakhotine, S., *Compt. rend.*, **200**, 2036 (1935); *Chem. Abs.*, **29**, 587 (1935); *Boll. soc. ital. biol. sper.*, **4**, 475 (1929); *Trans. Faraday Soc.*, **33**, 1068 (1937), *Compt. rend.*, **206**, 133 (1938).

¹⁶⁶ Fish, F., *Science*, **73**, 292 (1931); *Chem. Abs.*, **25**, 2771 (1931).

¹⁶⁷ Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.*, **61**, 272 (1922).

¹⁶⁸ Hinrichs, M., *Biol. Bull. Marine Biol. Lab.*, **50**, 55, 473 (1926).

¹⁶⁹ Klugh, A. B., *Canadian J. Research*, **1**, 100 (1929).

to light. It was concluded that there is a fairly close relation between the depth at which the organisms live and their susceptibility to radiations of shorter wave-lengths. In several cases lethal effects were found even though all the radiations used were present in sunlight.

Pigmented embryos of the nocturnal slug, *Limax flavus*, are easily injured by ultraviolet rays.¹⁷⁰ The deeply pigmented ones are especially sensitive.

The eggs and the first instar larva of the bean weevil, *Bruchus obtectus*, are killed by light of wave-lengths less than 3126Å.¹⁷¹ Adults showed no visible effects on irradiation, but most of their eggs were sterile. Sublethal doses produced weevils defective in metabolic processes.

Stevens¹⁷² found that total arc exposure of the whole *Ascaris* egg for six or eight hours usually did not kill the egg at once, but prevented further development if the eggs had been in the two-cell or four-cell stage at the time of exposure. With shorter exposures, there was observed irregular fragmentation of the chromosomes, delay in cleavage and abnormal gastrulation. Schleip¹⁷³ irradiated various parts of the egg separately and concluded that no one part could be affected without producing some alteration in the unirradiated parts as well. Ruppert¹⁷⁴ found a rhythmic alteration in the lethal effect, depending on the stage of development of the egg when irradiated with energy of a wave-length of 2800Å.¹⁷⁵

Wright and McAlister¹⁷⁶ found ova of the roundworm of the dog, *Toxascaris Leonina*, to exhibit retarded embryonation after irradiation with the lines 2652 or 2804Å at intensities of 684,000 ergs per sq. cm. They were particularly interested in the possible lethal action of sunlight, but found destructive effects only with the wave-length 3022Å, but not with longer ones. Even at 3020Å, 137,000,000 ergs per sq. cm., approximately equivalent to twelve days of July sunlight at Washington, D. C., caused only 1.5 per cent of the ova to reach embryonation, as compared with 42 per cent in the controls. For *Toxocara* ova, the corresponding figures were 20.5 per cent as compared with 65.5 per cent. The lesser susceptibility of this species may be due to absorption or dispersion of the light by the mosaically patterned, darkly pigmented shell of these eggs as compared with the clear, lightly pigmented shell of the *Toxascaris* ova. The ultraviolet rays of sunlight may be a factor, along with temperature and desiccation, in the marked lethal action of sunlight on ova reported by several workers.

APPLICATIONS

The Sterilization of Water. At one time sterilization by ultraviolet bid fair to be the method of choice for the treatment of water on a large scale and several installations were claimed to have been satisfactory. A description of the operation of an installation at Henderson, Ky., given by Smith,¹⁷⁷ states that there was little or no variation in the results, the rate of pumping being 2,200,000 to 3,200,000 gallons per day. The energy expenditure was said to have been 92.5 kilowatt hours per million gallons.

¹⁷⁰ Carmichael, E. B., *Physiol. Zool.*, 4, 575 (1931).

¹⁷¹ MacLeod, G. F., *Ann. Entomol. Soc. Am.*, 26, 603 (1933).

¹⁷² Stevens, N. M., *Arch. Entwicklungsmech. der Organismen*, 27, 622 (1909).

¹⁷³ Schleip, W., *Arch. Zellforsch.*, 17, 289 (1923).

¹⁷⁴ Ruppert, W., *Z. wiss. Zool.*, 123, 103 (1924).

¹⁷⁵ Note also Seide, J., *Z. wiss. Zool.*, 124, 252 (1925); *Chem. Abs.*, 20, 1871 (1926); Nolf, L. O., *Am. J. Hyg.*, 16, 288 (1932).

¹⁷⁶ Wright, W. H., and McAlister, E. D., *Smithsonian Misc. Coll.*, 93, 1 (1934).

¹⁷⁷ Smith, A. T., *Eng. News Record*, 1021 (1917).

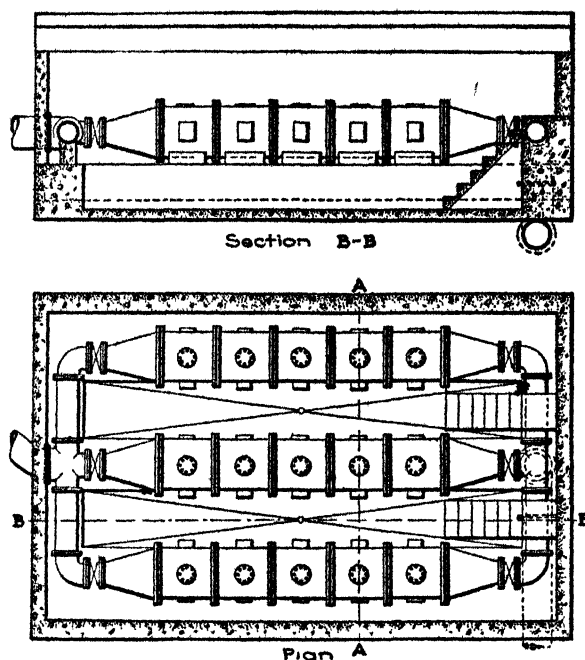


FIGURE 138 Large-scale Water Sterilization Equipment.

The ultraviolet sterilizers consisted of three legs each comprising five units. (Figure 138.) The legs were connected in parallel and the entire equipment was connected in series with a pipe line leading from the filtered water basin to the storage for the city supply. Each unit had a lamp box inserted in the side equipped with a clear quartz closed-end tube which projected into the body of the unit and around which the water was forced in a thin film by means of a baffle placed at 90° to the long axis of the sterilizer. The quartz tube was contained in a slotted opening in the baffle. (Figure 139.) The lamp

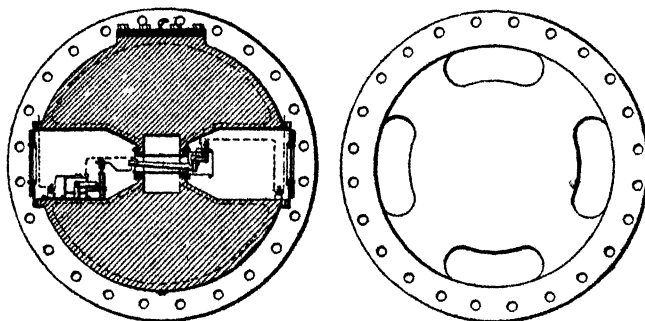


FIGURE 139. Lamp Box.

proper was a 220-volt d.c. mercury arc designed to be automatically tilted for starting by a special support located in the lamp box. The individual lamps were so connected that they could be adjusted individually. They were also connected to the main switch-board, each lamp having an incandescent lamp and a warning bell to notify the operator of improper operation.

Blocher¹⁷⁸ states that the method was successfully in use at Berea, Ohio, in 1929 for the treatment of river water. The water was passed through four copper boxes in series, each of which contained a mercury-vapor lamp surrounded by a quartz cylinder.¹⁷⁹

The advantages of the method are evident. The water itself undergoes no change. The materials in solution and the air, both of which give the water a pleasant taste, are retained. An overtreatment is not possible and the cost is not prohibitive. Springer,¹⁸⁰ although emphasizing that the water must first be clarified, believes the process to be superior to chlorination in that no disagreeable odor or taste is produced.¹⁸¹

Nevertheless, the method has declined in favor owing to the competition of the cheaper and in some respects simpler chlorination methods. For this reason working details of the apparatus employed will not be given, and reference will merely be made to the pertinent patents and articles in the field.¹⁸²

Beattie¹⁸³ states that the treatment of natural waters is ineffective. During the early development of these methods it was occasionally stated that the treatment of water so alters it as to render it germicidal. Such statements were disputed,¹⁸⁴ but have been occasionally found in the subsequent literature. Norton¹⁸⁵ stated that water exposed to ultraviolet light retained a slight germicidal power toward typhoid bacilli and Friedländer's bacilli, but not toward staphylococci.

The use of ultraviolet rays for the purification of the water of swimming pools is no longer practiced extensively, principally because of the inability to make the necessary exposure of all the water to the radiations. Also, chlorination is reported to be cheaper and more effective.¹⁸⁶ Occasionally a favorable report of the method still appears.¹⁸⁷

There are, however, several fields in which the method is useful because the chemical methods may be objectionable and an overdose harmful. Among these are the sterilization of water for surgical purposes under certain conditions, the sterilization of bottled waters, and other beverages (before bottling),¹⁸⁸ and the treatment of water intended for washing butter and for use in foods.¹⁸⁹

Lloyd¹⁹⁰ claims that the exposure of filtered sea water to ultraviolet light for

¹⁷⁸ Blocher, J. M., *J. Am. Water Works Assoc.*, **21**, 1361 (1929); *Brit. Chem. Abs.*, **1929B**, 1034.

¹⁷⁹ Note also Rodriguez-Ely, *Tech. sanit. munic.*, **30**, 288 (1935).

¹⁸⁰ Springer, J. F., *Pub. Works*, **62**, 10, 36; **11**, 65 (1931); *Chem. Abs.*, **26**, 1048 (1932).

¹⁸¹ See also Perkins, R. G., and Welch, H. [*Contract Journ.*, March 4, 1931; *Chem. Abs.*, **26**, 1997 (1932)] for a favorable opinion.

¹⁸² Helbronner, A., and von Recklinghausen, M., *British P.* 4,895; 24,632; 28,067; 25,883; 21,829; 30,397, Dec. 29, 1909; *French P.* 424,369. Henri, V., Helbronner, A., and von Recklinghausen, M., *U. S. P.* 1,140,819, May 25, 1915; 1,200,940; 1,150,117, Aug. 17, 1915; Dornic, P., and Daire, P., *Chem. Ztg.*, 936 (1909); *Chem. Abs.*, **3**, 2988 (1909); Tassilly, E., and Cambier, R., *Compt. rend.*, **151**, 342 (1910); *Eng. Record*, **110** (1912); *Sci. Am.*, **515** (1917); Otto, M. P., *French P.*, 421,296, Oct. 10, 1910; *J. für Gasbeleuchtung und Wasserversorgung*, **56**, 528 (1913); Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911); Nogier, T., *French P.* 426,606, May 6, 1910; 420,281; *British P.* 9,960, April 20, 1911; von Recklinghausen, M., *U. S. P.* 1,156,947, Oct. 19, 1915; 1,193,209; *J. Soc. Chem. Ind.*, 976 (1916); Parkinson, N. F., *23rd. Ann. Rept. of Provincial Board of Health, Ontario, Canada*, **33**, 156 (1914); Keyes, F. G., *U. S. P.* 1,235,698, Aug. 7, 1917; Brûère, S., *Ann. Hyg. Pub. New Series*, **1**, 348 (1923); Dienert, F., *Ann. Hyg. Pub. Ind. Sociale*, 586 (1924); Sirch, C. W., *U. S. P.* 1,860,435, May 31, 1932; Baumgärtel, T., *Wasser und Abwasser*, **33**, 207 (1935); *Chem. Abs.*, **29**, 6677 (1935).

¹⁸³ Beattie, J. M., *Surveyor*, **78**, 69 (1930); *Chem. Abs.*, **26**, 1365 (1932).

¹⁸⁴ Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910).

¹⁸⁵ Norton, J. F., *Am. J. Pub. Health*, **18**, 476 (1928); Vadimov, M., *Priroda*, **24**, No. 4, 13 (1935); *Chem. Abs.*, **31**, 7074 (1937).

¹⁸⁶ See Heath, R. F., *Can. Engr.*, **70**, No. 14, 27 (1936); *Chem. Abs.*, **30**, 7746 (1936).

¹⁸⁷ Turner, A. A., *J. Roy. Sanit. Inst.*, **55**, 441 (1935); *Chem. Abs.*, **30**, 1481 (1936).

¹⁸⁸ Schneegg, H., Kipphan, H., and Grunert, K., [*Z. ges. Brauw.*, **59**, 21 (1936); *Chem. Abs.*, **30**, 8513 (1936)] discuss its use in breweries.

¹⁸⁹ Stateler, E. S., *Food Ind.*, **7**, 535 (1935).

one second sterilizes it effectively. The cost of irradiation treatment is said to be about a hundred times that of chlorination.¹⁰¹

Residual chlorine and chloramine in distilled water drop markedly on exposure of the water to arc lamps, and the acidity increases in proportion to the reduction in free chlorine.¹⁰² The *o*-tolidine reagent used in the free chlorine test becomes unreliable because of discoloration after exposure to direct sunlight for two months. Similar discoloration impairs the dichromate-copper sulfate standard.¹⁰³

STERILIZATION OF FOOD PRODUCTS

Sterilization of Milk and Other Opaque Substances. After the introduction of ultraviolet sterilization, many patents describing processes for treating milk were issued. These will not be described in detail since the process apparently interferes with the irradiation of milk for the production of vitamin D, and because complete sterilization is difficult. Also the prolonged treatment necessary for sterilization is reported to have deleterious effects upon the flavor of the milk.¹⁰⁴ In the patent of Henri and von Recklinghausen, it was stated that heating the milk to 60°C. before irradiation would make the bacteria more sensitive to the action of the rays. In addition to the preheater (Figure 140) there was employed a rotating

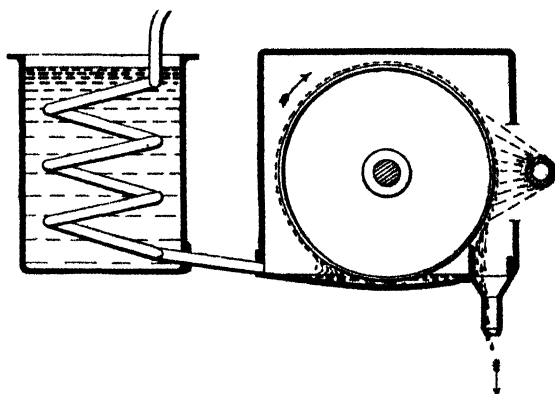


FIGURE 140. Apparatus of Helbronner and von Recklinghausen for Heat and Ultraviolet Treatment of Milk.

drum to pick up a very thin film of the milk, a procedure frequently used in irradiation of opaque fluids. von Recklinghausen¹⁰⁵ obtained a thin film by passing the liquid between two plates, one of quartz, the plates being separated by sheets of tin foil. Further patents dealt with details of methods for removing milk from rotating drums or rollers in such a manner as to avoid formation of particles of butter on the roller.¹⁰⁶

¹⁰⁰ Lloyd, B., *J. Roy. Tech. Coll.*, **3**, 505 (1935); *Chem. Abs.*, **29**, 4041 (1935).

¹⁰¹ Vagedes, H., *Gas-und Wasserfach*, **78**, 80 (1935); *Chem. Abs.*, **32**, 1826 (1938).

¹⁰² Buchanan, E. B., and Dodge, J. K., *15th Ann. Rept. Ohio Conf. Water Purif.*, **40** (1936); *Chem. Abs.*, **30**, 6859 (1936).

¹⁰³ Davis, W. S., and Kelly, C. B., *J. Am. Waterworks Assoc.*, **26**, 757 (1934); *Chem. Abs.*, **28**, 4807 (1934).

¹⁰⁴ Henri, V., and von Recklinghausen, M., U. S. P. 1,141,046, May 25, 1915.

¹⁰⁵ von Recklinghausen, M., U. S. P. 1,165,921, Dec. 28, 1915; *Chem. Abs.*, **10**, 649 (1916).

¹⁰⁶ Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,140,818, May 25, 1925; 1,068,898, July 29, 1913; 1,052,818, Feb. 11, 1913; Helbronner, A., and von Recklinghausen, M., *Brit. Pat.* 12,948, May 27, 1910; 18,458, Aug. 4, 1910; for sterilizing fats and butter, note Soc. Le Serment, French P. 400,921, March 17, 1909.

Potencier¹⁹⁷ delivers milk under carbon dioxide pressure from a tank onto a metal or transparent table in a thin layer and collects the milk in a gutter surrounding the table. The rays are emitted from tubes situated under a parabolic cupola above the table. The cupola may be made either of polished metal or of insulating material faced on the inside with a fluorescent coating yielding rays between 2300 and 4500Å. Scheidt¹⁹⁸ used a lamp in which a high-tension discharge is passed through neon and argon in a series of quartz tubes either U-shaped or formed of two coaxial vertical rims one enclosing the other. The rays are allowed to act on the liquid as it flows in a thin film between the surfaces of the quartz tubes and surrounding tubes of porcelain.

Vogeler¹⁹⁹ states that sterilization of milk by ultraviolet light is not a feasible process. Various attempts have been made to combine the use of ultraviolet rays with chemical treatments, using for example, hydrogen peroxide²⁰⁰ or chlorine.²⁰¹

*Food Products.*²⁰² The ingredients of jams, jellies, and other preserves may be subjected to the action of ultraviolet rays while being heated in a shallow pan provided with means for agitation and removal of the scum.²⁰³ Perino²⁰⁴ suggested that nutritive extracts of vegetables be irradiated in the absence of oxygen.

Spolverini²⁰⁵ states that ultraviolet irradiation of certain foods causes physical and chemical changes which tend to aid conservation. Berndt and Creighton²⁰⁶ treat the foodstuff with ultraviolet until beneficial properties have been imparted to a portion of the material, and mix this with untreated material. Apparatus designed for irradiation of viscous food products such as malt extracts has been described by Rohde.²⁰⁷ Duret²⁰⁸ finds ultraviolet sterilization of sugar solutions of value because occasional samples of sugar are found to contain thermophilic bacteria which resist heat sterilization.

Ultraviolet Sterilization in Baking Industry. In milling flour, it is usually necessary to remove the germ from cereals in order to prevent growth of organisms which lead to spoilage of the flour. To preserve these valuable portions of the grain, Mayor²⁰⁹ proposes to irradiate the germ with ultraviolet rays, roast the treated germ, and mix the latter with the ground kernel of the same or other cereal.

In the bleaching of flour, mercury-arc irradiation is occasionally employed to supplement the action of such bleaching agents as dibenzoyl peroxide. By this means it is said to be possible to obtain in one hour the amount of bleaching that

¹⁹⁷ Potencier, R., British P. 430,908, Dec. 21, 1933; *Brit. Chem. Abs.*, B, 827 (1935).

¹⁹⁸ Scheidt, E. O., British P. 257,956, Sept. 6, 1926; *Brit. Chem. Abs.*, B, 106 (1928); U. S. P. 1,670,217, May 15, 1928.

¹⁹⁹ Vogeler, L., *Milchwirtschaft Literaturber.*, 484 (1930); *Chem. Abs.*, 26, 1039 (1932).

²⁰⁰ Bing, M., German P. 392,935, 1922; *Brit. Chem. Abs.*, B, 345 (1927).

²⁰¹ Tranin, S., and Snyder, R. M., U. S. P. 1,945,102, Jan. 30, 1934; *Chem. Abs.*, 28, 2428 (1934). Note for another recent milk patent, Castelain, L., U. S. P. 1,956,667, May 1, 1934.

²⁰² See Haines, R. B., Lea, C. H., Lea, D. E., and Tompkins, R. G., *Rep. Food Invest. Bd.*, 29, 1936; *Brit. Chem. Abs.*, B, 1264 (1937).

²⁰³ McKinlay, D., British P. 273,578, Dec. 14, 1926; 272,775 (for fruits); cf. Mayor, J., U. S. P. 1,911,913.

²⁰⁴ Perino, J., British P. 279,487, Oct. 22, 1926; *Chem. Abs.*, 22, 2799 (1928).

²⁰⁵ Spolverini, L. M., *Riv. ital. actionol.*, 2, 1 (1927); *Chem. Abs.*, 23, 4508 (1929).

²⁰⁶ Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8; *Chem. Abs.*, 31, 2701 (1937).

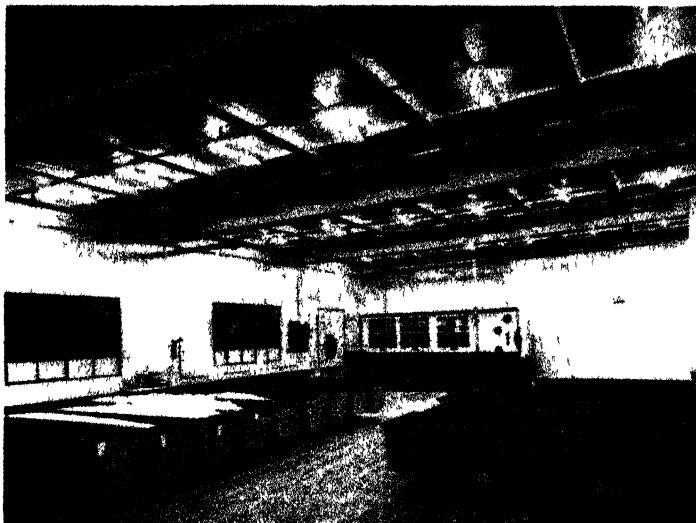
²⁰⁷ Rohde, H. W., U. S. P. 1,888,472, to Jos Schlitz Beverage Co.

²⁰⁸ Duret, G., French P. 736,254, Aug. 13, 1931; *Chem. Abs.*, 27, 1540 (1933); British P. 395,527, July 20, 1933; *Chem. Abs.*, 28, 362 (1934).

²⁰⁹ Mayor, J., French P. 752,261, Sept. 20, 1933; *Chem. Abs.*, 28, 838 (1934).

would be effected by allowing the peroxide to stand alone in contact with flour for 48 hours.²¹⁰

Read²¹¹ studied the use of various sources of ultraviolet light in killing mold spores infecting the surface of freshly baked bread. He did not find the mercury⁴ vapor arc to offer the advantages to be obtained by the use of the carbon arc. With various carbons, the fungicidal potency decreases in the following order: "C," "U," "K" and Mg. On the other hand it has been stated that growth of molds in bread can be checked by utilization of discharge lamps containing argon, neon and mercury.²¹² Rooms in which dough is stored for yeast reaction are kept



Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 141. Use of Ultraviolet Radiation in Dough Room of a Bakery.

warm and moist and these conditions favor the growth of molds. It was reported that such growth could be inhibited by exposing dough to lamps emitting radiation between 2000-2600Å. The rays were said not to penetrate beneath the surface of the dough, and to have no effect upon the yeasting process (Figure 141). Also, lamps which furnish rays in the range mentioned have been employed in the cooling and wrapping rooms of bakeries to prevent deposition of bacteria on bread subsequent to the baking process. Bonsor²¹³ subjected the dough ingredients during mixing to ultraviolet light for five or ten minutes to render the final product lighter and more easily digested.

²¹⁰ Ferrari, C. G., and Croze, A. B., *Cereal Chem.*, 11, 505 (1934); *Chem. Abs.*, 29, 236 (1935); Ferrari, C. G., Croze, A. B., and Bailey, C. H., *Cereal Chem.*, 9, 491 (1932); *Chem. Abs.*, 26, 6027 (1932); Sutherland, E. C., U. S. P. 1,539,701, May 26, 1925; *Chem. Abs.*, 19, 2246 (1925); British P. 249,139, March 11, 1925; 102,967, Dec. 22, 1915; *Chem. Abs.*, 11, 1219 (1917); U. S. P. 1,381,079, June 7, 1921; 1,380,334, May 31, 1921; *Chem. Abs.*, 15, 3349 (1921); Gelissen, H., U. S. P. 1,483,546, Feb. 12, 1924; *Chem. Abs.*, 18, 1167 (1924). In the earlier patents, other oxidizing agents, usually peroxides, were suggested.

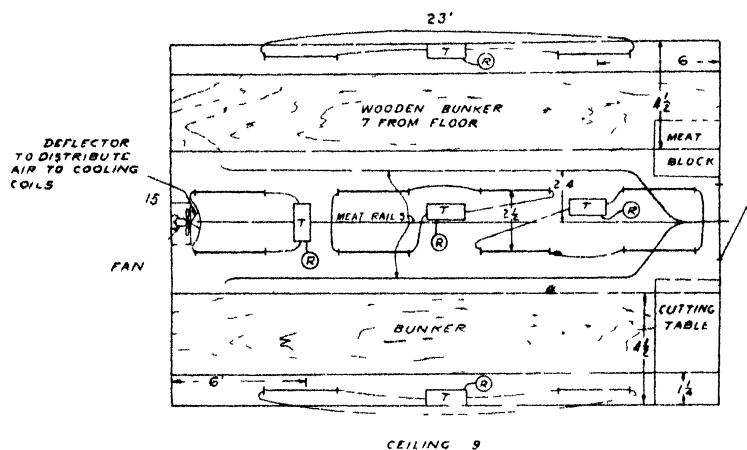
²¹¹ Read, J. W., *Cereal Chem.*, 11, 80 (1934); *Chem. Abs.*, 28, 3142 (1934).

²¹² Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Garrett, O. F., and Arnold, R. B., *Milk Plant Monthly*, August (1938). *Food Industries*, 10, (5), 263 (1938). James, R. F., *Food Industries*, 10 (6), 295 (1936). Dennington, A. R., *The Bakers Technical Digest*, March (1937). Broadbent, H. S., *Food Industries*, 10 (6) (1938).

²¹³ Bonsor, S., British P. 280,729, Dec. 16, 1926; *Brit. Chem. Abs.*, B, 106 (1928).

Ultraviolet Sterilization in Meat Industry.²¹⁴ Freshly slaughtered beef is composed of small muscle fibers 0.002 inch in diameter and 1 to 2 inches in length enclosed in a sheath-like covering. The muscle fibers are bound together into larger aggregates by connective tissue. When beef is stored, the connective tissue is changed to a gelatin by enzymic action within the meat. This process, called tendering, may be accelerated by increasing the temperature. However, temperatures above refrigeration limit (above 45°F.) also speed up mold formation on the surface of the meat, thereby causing considerable loss of the latter when the mold is cut away.

Also, storing of meat may result in considerable shrinkage by evaporation of moisture when the relative humidity of the storage room is below 83 per cent. A relative humidity of 85-90 per cent in the vicinity of stored meat was stated to prevent evaporation from meat to a large extent. These highly moist conditions tend to accelerate mold formation.



CEILING 9
Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 142. Use of Ultraviolet Lamps in Meat Storage Rooms.

The presence in a storage room of rays of about 2000-2600Å was advocated as effective in inhibiting mold formations on meat surfaces, at temperatures above 35°F. and relative humidity of 85-90 per cent.²¹⁵ Lamps emitting these radiations generally are placed in rows parallel to the racks or rails on which meat is hung for storage or tendering (Figure 142). Also, it is reported that circulation of air in the storage room prevents mold formation in areas where meat is not exposed directly to rays from discharge lamps.

Miscellaneous Applications. Ultraviolet sterilization has been proposed as efficient for destroying bacteria on eating and drinking implements.²¹⁶ Exposure of glasses (after washing and rinsing) to rays from discharge lamps was reported to result in destruction of 87-100 per cent of the bacteria present.

²¹⁴ Ewell, A. W., *Refrigerating Engineering*, January (1939). Coulter, M. D., Address at Mellon Institute of Industrial Research, March 21, 1939. British P. 22,669, 1914, to Monvoisin, Barrat et Robin; *Chem. Abs.*, 10, 1238 (1916).

²¹⁵ Lamps utilized for this purpose are known as Sterilamps (Trade Mark Registered U. S. Patent Office), manufactured by Westinghouse Electric & Manufacturing Co.

²¹⁶ R. V. Fellers, *The American City*, August, 53 (1938).

In the sterilization of fruit juices, Welch and Perkins²¹⁷ suggested the use of the photosensitizing action of eosin or fluorescein, only very small concentrations being required.

The condition of pitched barrels or casks is reported to be greatly improved, even though complete sterilization is not attained, by lowering quartz lamps into them and irradiating them for fifteen to thirty seconds. Longer periods may heat the casks to such an extent as to cause the liberation of the fumes of pitch.²¹⁸

STERILIZATION OF MEDICINAL PRODUCTS

Vaccines. It was early proposed to treat vaccinia virus by ultraviolet rays, the belief being that harmful foreign organisms could be killed by doses insufficient to destroy the more resistant virus.²¹⁹ Kirstein,²²⁰ using the Vitaray apparatus,

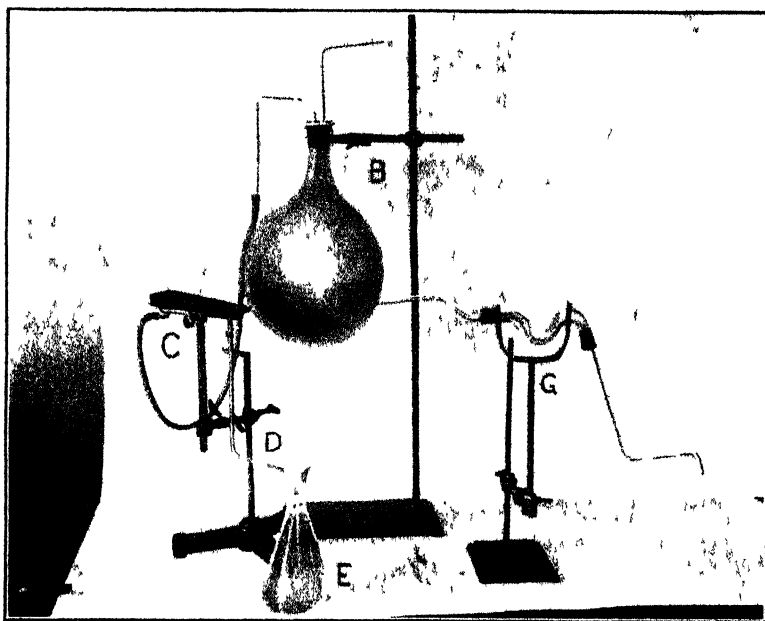


FIGURE 143 Apparatus of Houghton and Davis for Sterilization of Vaccines.

was unable to find any evidence of such action. Later, however, he introduced a process using a salicylic acid filter, which he claimed accomplished this purpose not in the case of the vaccinia virus, but in the preparation of various bacterial vaccines. The killing of the organisms was said to be accomplished by filtered ultraviolet rays.²²¹

²¹⁷ Welch, H., and Perkins, R. G., *J. Prev. Med.*, **5**, 173 (1931), *Chem. Abs.* **26**, 5362 (1932).

²¹⁸ *Sci. Am.*, 201, Aug. 28, 1920; Moufang, E., *Allgem. Z. Bierbrau. Malsfab.*, **43**, 151 (1915).

²¹⁹ German P. 314,858, Feb. 24, 1914, to Quarzlampen Ges. Hanau, *J. Soc. Chem. Ind.*, **39**, 312 (1920); Friedberger, F., and Miunescu, E., *Deut. Med. Wochschr.* 1203 (1914), Mayerhofer, E., *Z. Kinderheilk.*, **13**, 361 (1916).

²²⁰ Kirstein, F., *Zentralb. Bakt. Parasitenk. Infektionsk.*, **I**, 114, 530 (1929).

²²¹ Kirstein, F., German P. 598,680, June 15, 1934, *Chem. Abs.*, **28**, 5932 (1934), German P. 600,941, Aug. 3, 1934; *Chem. Abs.*, **28**, 7433 (1934), German P. 609,258, Feb. 11, 1935, *Chem. Abs.*, **29**, 6366 (1935). Note also Mayer, G., German P. 505,707, April 3, 1927, *Chem. Abs.*, **25**, 382 (1931).

Figure 143 illustrates apparatus used by Houghton and Davis²²² for sterilizing bacterial vaccines and other products. The material to be irradiated is contained in a glass flask B connected by a sterile glass siphon and rubber tubing to the trough C placed directly beneath the arc. After exposure in the trough, the liquid passes through the delivery tube D into a previously sterilized container E. A modern quartz mercury arc suitable for irradiating the liquid in the trough is shown in Figure 144.



Courtesy Dr. L. J. Buttolph, Lamp Department, General Electric Co.

FIGURE 144. Modern Quartz Mercury Arc for Irradiation of Liquids.

Pharmaceutical Products. Lesure²²³ found it possible to sterilize several drug preparations without altering them, although in several cases the absorption by the drugs was so great as to prevent effective sterilization within a reasonable time. Silver nitrate, eserine salicylate, apomorphine hydrochloride and atoxyl all became colored after five minutes of exposure and morphine hydrochloride, arbutin and guaiacol cacodylate after fifteen to thirty minutes. Arbutin became colored after three hours because of the formation of quinol and its oxidation products.

Sperti, Norris, Withrow and Schneider²²⁴ proposed to employ only selected radiations, obtained by the use of filters of, for example, lead acetate, in destroying bacteria in enzyme solutions without affecting the enzyme activity. They also suggested that selective irradiation might be employed for activation of vitamins and for differentially affecting organic substances having several ingredients.

Mingoia²²⁵ found it impossible to sterilize solutions of such alkaloids as heroine, cocaine, atropine and codeine by irradiation so as to render them suitable for hypo-

²²² Houghton, E. M., and Davis, L., *Am. J. Public Health*, 4, 224 (1914).

²²³ Lesure, A., *J. pharm. chem.*, 1, 569 (1910); *J. Chem. Soc.*, 98, 739 (1910).

²²⁴ Sperti, G., Norris, R. J., Withrow, R., and Schneider, H., U. S. P. 1,676,579, July 10, 1928

²²⁵ Mingoia, Q., *Ann. chim applicata*, 23, 318 (1933); *Chem. Abs.*, 27, 5889 (1933).

dermic use without at the same time altering the alkaloids seriously. Nitzescu²²⁶ believed that insulin solutions could be sterilized in this manner.²²⁷

Kelly²²⁸ proposed the sterilization by irradiation of certain emulsions used in ointments and shaving creams.

In treating substances serving as sources of essential oils, Tival and Descombes²²⁹ first froze the material, then irradiated it and dried it *in vacuo* before extracting the oil. Rousseau²³⁰ added uranium, iron or manganous salts to enzymes or yeast before subjecting the latter to the action of ultraviolet rays.

According to Stevens,²³¹ ultraviolet light renders the lipids of skin, extracted and emulsified in salt solution, bactericidal to hemolytic streptococci. It increases markedly the active oxygen content of dried skin, unless the lipids had been extracted before irradiation.

Various Products. Wool which has been treated with ultraviolet light is said²³² to have increased susceptibility to mold growth. Gelatin solutions and articles made from them, such as threads, cords, violin strings, ribbons, or tubes, may be sterilized by ultraviolet light, according to Hirsch.²³³ Redd²³⁴ describes apparatus for subjecting clothes to ultraviolet rays and ozone in laundry apparatus.

Lehmann²³⁵ finds that staphylococci in contact with linoleum die more rapidly under strong illumination than when irradiated on glass or wood. This is ascribed to the action of oxidation products of the linseed oil present in the linoleum.

Considerable attention has recently been devoted to the bactericidal properties of irradiated petrolatum. Eising²³⁶ noted that the latter exerted a strong bactericidal action upon the ordinary organisms of wound infection and believed it also to stimulate the processes of healing. Sheard and Thompson²³⁷ found irradiated mineral oil less active than irradiated olive oil or Vaseline. Harris, Bunker and Milas²³⁸ found the vapors of certain oils to inhibit or kill bacterial smears on nutrient agar without irradiation, although other oils acquired this power only after being irradiated. They believed the germicidal action due probably to volatile substances containing peroxidic oxygen in the oil, the formation of which is accelerated by irradiation, the most effective rays being about 3130Å. In general, animal oils were more active than vegetable oils. The germicidal properties are not the result of secondary radiations, aldehydes, butyric acid or ozone. Sears and Black²³⁹ observed that white petrolatum becomes germicidal after four hours of irradiation and changes to a limpid yellow color. The germicidal agent is believed to be a non-volatile chemical substance, not water-soluble, formed as the result of oxidation. It does not kill spores or certain gram-negative intestinal organisms. Stevens²⁴⁰

²²⁶ Nitzescu, I. I., *Klin. Wochschr.*, 3, 2343 (1924); *Chem. Abs.*, 19, 1285 (1925).

²²⁷ See, however, Chapter 34.

²²⁸ Kelly, T. D., *British P.* 283,711, Dec. 13, 1926; *Chem. Abs.*, 22, 4205 (1928).

²²⁹ Tival, H., and Descombes, F., *British P.* 179,164, April 25, 1922; *Chem. Abs.*, 19, 1019 (1925).

²³⁰ Rousseau, E. F., *British P.* 226,534, Dec. 17, 1923; *Chem. Abs.*, 19, 2103 (1925).

²³¹ Stevens, F. A., *J. Exptl. Med.*, 65, 121 (1937).

²³² Burgess, R., *J. Soc., Dyers Colourists*, 50, 138 (1934); *Chem. Abs.*, 29, 1992 (1935).

²³³ Hirsch, P., *British P.* 299,105, July 25, 1927; *Chem. Abs.*, 24, 3061 (1929).

²³⁴ Redd, W. R., U. S. P. 1,948,239, Feb. 20, 1934, to Millprint Products Corp.; *Chem. Abs.*, 28, 2923 (1934).

²³⁵ Lehmann, K. B., *Arch. Hyg.*, 106, 1 (1931); *Chem. Abs.*, 26, 166 (1932).

²³⁶ Eising, E. H., *Annals of Surgery*, 93, 1231 (1931); *British P.* 417,685, Oct. 10, 1934; *Chem. Abs.*, 29, 1211 (1935). U. S. P. 1,919,055, July 18, 1933; *Chem. Abs.*, 27, 4879 (1933).

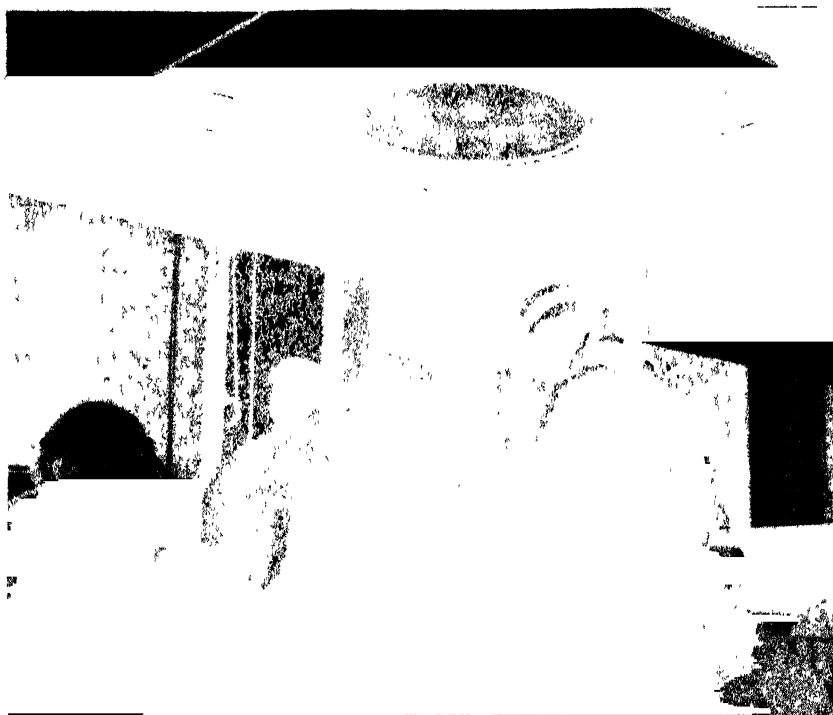
²³⁷ Sheard, C., and Thompson, L., *Proc. Staff Meeting Mayo Clinic*, 6, 690 (1931); *Chem. Abs.*, 26, 2764 (1932).

²³⁸ Harris, R. S., Bunker, J., and Milas, N., *J. Bact.*, 23, 429 (1932); *Ind. Eng. Chem.*, 24, 1181 (1932).

²³⁹ Sears, H. J., and Black, N., *J. Bact.*, 27, 453 (1934).

²⁴⁰ Stevens, F. A., *J. Lab. Clin. Med.*, 21, 26, 1040 (1935-6); *J. Bact.*, 32, 47 (1936); *J. Inf. Dis.*, 58, 185 (1936).

attributed the photoactivity of such products to the evolution of gaseous organic peroxides and aldehydes which diffuse rapidly through a film of cellulose acetate. The plate-fogging and bactericidal effects of the vapor from irradiated cod-liver oil and from ozonide of olive oil were found to be due to substances liberating active oxygen. Not only are bacteria killed by the oxygen liberated from these oils, but their growth rate may be retarded or dissociation may occur if the organisms are subjected to sublethal doses.



Courtesy Westinghouse Electric and Manufacturing Co

FIGURE 145. Ultraviolet Sterilization of Air in Operating Room.

Reiner-Deutsch and Molnar²⁴¹ found irradiation of essential oils in alcohol for fifteen minutes at 25 cm. from a Burdick air-cooled lamp to increase their bactericidal power so that the vapors would kill staphylococci in three hours.

It has been claimed that irradiated metals are bactericidal at a distance²⁴²

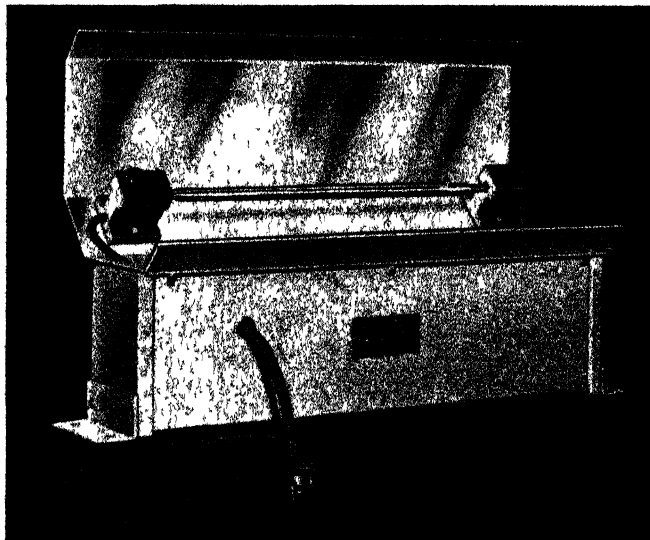
*Utilization of Ultraviolet Sterilization in Hospitals.*²⁴³ The degree of contamination in an operating room is said to depend on the duration of occupancy, number of occupants in the room, the number of contamination carriers and the degree

²⁴¹ Reiner-Deutsch, W., and Molnar, N., *J. Bact.*, **30**, 444 (1935); *Chem. Abs.*, **30**, 1086 (1936).

²⁴² Ried, O., *Centralbl. Bakt. Parasitenk., Abt. I*, **121**, 267 (1931); Goldberg, I. M., *Acta. Med. Scand.*, **83**, 212, 573 (1934).

²⁴³ Hart, D., *J. Thoracic Surg.*, **6** (1), 4581 (1936). Hart, D., *Surgery*, **1** (5), 770 (1935). Hart, D., *Archives of Surgery*, **34**, 874 (1937). Hart, D., and Gardner, C. E., Jr., *Transactions of the Southern Surgical Association*, **49**, 377 (1937). Hart, D., *J. Thoracic Surg.*, **7** (5), 525 (1938). Hart, D., *Archives of Surgery*, **37**, 956 (1938). *The Modern Hospital*, **46** (6), June (1936). Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938).

of contamination in their respiratory passages, the adequacy of masks, the cleanliness of the room and of the incoming air, and the efficacy of the ventilating system. It was found that careful regulation of the above factors to afford maximum protection against entrance of bacteria did not achieve this purpose completely. Members of the operating team constantly breathe bacteria into the air, even though all members wear masks. Presence of bacteria is particularly dangerous in thoracic surgery, where long incisions are made. For this reason, thoracic operations seldom were performed during winter months, when the probability of respiratory contamination in the operating team was highest. The observations of Rentschler and James²⁴⁴ that air-borne pathogenic bacteria can be killed with about 10 per



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 146 Operating Room Safe-T-Aire Equipment for Ceiling or Wall Mounting.

cent of the radiant energy required to kill the same bacteria on a plate led to a method for controlling bacteria in operating rooms. In one type of installation proposed by James and Hart (Figure 145) a bank of eight lamps which emit principally the line 2537A is arranged in a square above the operating table. Rays from these lamps kill bacteria (breathed by members of the operating team) before the bacteria reach the body of the patient. It was stated that the intensity of the ultraviolet rays reaching the operating table is too low to cause harmful after-effects to the patient. Further, utilization of such lamps was reported to accelerate wound healing.

The effectiveness of bactericidal radiation during extrapleural thoracoplasties has been studied. It was found that mortality was reduced more than 50 per cent by use of radiation during operations, that postoperative infection was avoided almost completely, that postoperative temperature elevations of patients decreased and that wound healing was more rapid. Also, the period required before reopen-

²⁴⁴ Rentschler, H. C., and James, R. F., in article of Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Rentschler, H. C., Address at Mellon Institute of Industrial Research, March 21, 1939.

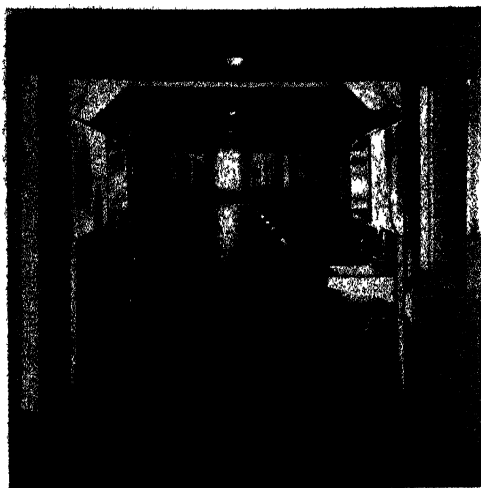


FIGURE 147 (a).

Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 147 (b).

Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.

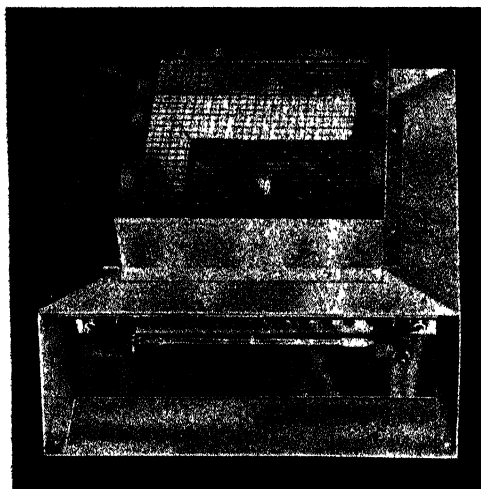
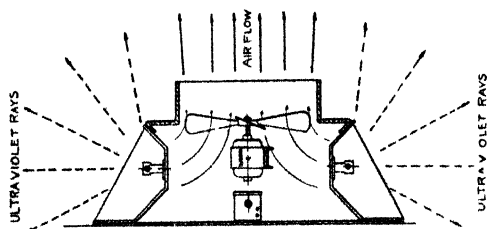


FIGURE 147 (c).

Courtesy Hanovia Chemical and Manufacturing Co.

ing of the wound to complete the stages of thoracic surgery was reported to be lessened considerably.

Wells and Brown²⁴⁵ found it possible by means of the mercury arc to destroy the infectivity for ferrets of the influenza virus (P R 8 strain) suspended in air. Other quartz operating room lamps have been designed (Figure 146) for ceiling or wall mounting. "Baryaire" units (Figure 147) have been devised for use in hospital corridors to prevent cross-infection. It is claimed that microorganisms cannot be carried past the barrier of ultraviolet light.²⁴⁶

²⁴⁵ Wells, W. F., and Brown, H. W., *Am. J. Hyg.*, 24, 407 (1936); see also Wells, W. F., and Wells, M. W., *J. Am. Med. Assoc.*, 107, 1698, 1809 (1936).

²⁴⁶ Note also Magondeaux, B., French P. 729,022, March 9, 1932.

Chapter 36

The Physiological Effects of Ultraviolet Rays

The success attained in the use of ultraviolet light in the treatment of rickets, surgical tuberculosis and certain other conditions discussed in subsequent chapters, stimulated a widespread empirical (and frequently non-critical) use of this treatment for a great variety of diseased conditions. Unwarranted and extravagant claims served to create an undeserved prejudice against even the proper application of this form of therapy. For this reason, before discussing in Chapter 38 the therapeutic applications in which ultraviolet light may serve a useful purpose, it is desirable to consider the present state of our knowledge of the general physiological effects of this form of energy upon multicellular organisms. The preceding chapters have laid the basis for this by enumerating the effects of the rays upon the chemical constituents of cells and upon individual cells as a whole. The way in which generalized irradiation of large areas of the body may produce alterations in the circulation, respiration, the composition of the blood and the growth of the body as a whole or of various of its organs may now be considered.*

In the extensive literature many apparent contradictions abound.

In part, these may be ascribed to inaccurate observations or to too hasty generalizations from an inadequate number of experiments. In part, they are due to a failure to appreciate the necessity of controlling the spectral distribution of the sources employed. Much work calls for repetition under more adequate physical control. In the present survey, it has not been considered possible to undertake a detailed analysis of the adequacy of the experimental approach in the various investigations reported, since for the most part the results are not usually striking. A more critical treatment would demand a much larger amount of space than is justifiable in view of the fact that there are at present available several reviews and books. Only an outline of what appear to be the more significant conclusions is given here.¹

Comparatively little work has as yet been done on the application of the Einstein law to biological systems, aside from that involved in the photosynthetic mechanism in plants and in the formation of vitamin D₂.² There is thus a hiatus between the photochemical theories discussed and applied in Part II of this book and the treatment of the photochemical processes upon which must ultimately depend the physiological responses which occupy a large part of the remainder of this book.

Early workers were inclined to the belief that ultraviolet rays act in some manner by virtue of photoelectric effects, produced when they strike the living organ-

* The conversion of sterols into vitamin D and its application is deferred to Chapters 38, 39 and 40.

¹ Laurens, H., "The Physiological Effects of Radiant Energy," American Chemical Society Monograph Series, New York, Reinhold Publishing Corp., 1933; "The Biological Effects of Radiation," Edited by Duggar, B. M., 2 Vols., New York, McGraw-Hill Book Company, Inc., 1936.

Review articles: Valentin, H., *Pharm. Ztg.*, **75**, 982, 995, 1005 (1930); *Chem. Abs.*, **25**, 120 (1931); Levine, V. E., *Arch. Phys. Therapy, X-Rays & Radium*, **12**, 197, 267, 389 (1931); Packard, C., *Quart. Review Biol.*, **6**, 253 (1931); Snyder, C. D., *Ibid.*, 281; Frankenburger, W., *Strahlentherapie*, **21**, 233 (1933); de Toni, G., *Biochim. terap. sper.*, **22**, 547, 577 (1935); **23**, 75 (1936).

² Warburg, O., *Trans. Faraday Soc.*, **27**, 551 (1931).

ism.³ This is now recognized to play a role of importance only when the wavelengths employed are far shorter than those available from the sources usually employed under the ordinary conditions of experimental work or practical therapy.⁴

Attention has been drawn by various workers to the possibility that x-rays or radium may owe some of their biological actions to ultraviolet rays produced as a result of the fluorescence of some components of the irradiated systems. As yet this possibility has been relatively little explored.⁵

There have been, among the many suggestions advanced to account for the general reactions underlying the utility of heliotherapy or artificial ultraviolet therapy, a few which have attained special prominence, at least for a time. One group of workers advanced the claim that the effects were due, not to the direct effects of the light rays upon the body surface, but rather to the production in the air of ozone or oxides of nitrogen which when breathed were indirectly responsible for the effects produced. A leading sponsor of this theory was Kestner,⁶ who had in mind particularly the use of a carbon arc source. Peemöller⁷ asserted that only when the air through which the rays passed was breathed was it possible to observe any effect of the irradiation upon the blood pressure. This theory has been discredited by subsequent workers who have shown that the effects of irradiation on blood pressure cannot be detected if the subject (a dog) is exposed to the irradiated air but protected by filters from the direct action of the rays.⁸

Another view was that physiological alterations may ensue as a result of a stimulation through the eye of the nervous control of the circulation. There is an experimental basis for this in the observation by Reed that in the dog⁹ strong irradiation of the retina produces a depression of the blood pressure, usually accompanied by a decrease in the heart rate, which eventually leads to a condition of shock unless the irradiation be discontinued. Nevertheless, there is little reason to believe that under ordinary conditions the reaction of the body to irradiation is brought about by nerve stimulation in the eye and this may be dismissed from further consideration.

Current theories regard the behavior as a response to changes brought about in the skin. Most of the radiations are absorbed in very thin layers of the skin and do not penetrate to the lower tissues. One process which occurs in the skin, the conversion of certain sterols into the vitamins of the D group is definitely known to account for the beneficial results of irradiation in the prevention and treatment of rickets, and there is an accumulating body of evidence that this may also account, in part at least, for the beneficial results in tuberculosis. There are, however, undoubtedly other processes induced in the skin which are less well understood. The visible changes in sunburn have been attributed to the production of histamine-like materials which then act upon the vessel walls and produce the local erythema. Such substances may enter the blood stream and be carried to the nervous tissues which control the fundamental physiological processes. Such substances may also conceivably exert a control through a local stimulation of certain afferent nerves. Viale and Roncallo¹⁰ find that although irradiation of a normal

³ Clark, J., *Physiol. Rev.*, **2**, 277 (1922).

⁴ See, however, Saidman, J., *Compt. rend.*, **180**, 693 (1925); Gallerani, G., *Boll. soc. ital. biol. sper.*, **11**, 817 (1936); *Chem. Abs.*, **31**, 7759 (1937).

⁵ See Spiegel-Adolf, M., *Klin. Wochschr.*, **9**, 1615 (1930).

⁶ Kestner, O., *Z. Biol.*, **73**, 1, 7 (1921); **77**, 245 (1922).

⁷ Peemöller, F., *Klin. Wochschr.*, **2**, 973 (1923); note also Secchi, C., *Pediatria Rivista*, **35**, 1111 (1927); *Chem. Abs.*, **22**, 1786 (1928).

⁸ Laurens, H., and Mayerson, H. S., *Am. J. Physiol.*, **84**, 524 (1928).

⁹ Reed, C. I., *Am. J. Physiol.*, **65**, 477 (1923).

¹⁰ Viale, G., and Roncallo, E., *Boll. soc. ital. biol. sper.*, **10**, 311 (1935); *Chem. Abs.*, **30**, 6014 (1936).

rabbit's foot depresses the blood sugar, this effect is not found if the nerves to the foot are first cut. Furthermore, section of the right vagus nerve at the neck also interferes with the fall in blood sugar which usually follows irradiation.¹¹

Other views assume that light absorbed by the blood in dilated skin capillaries alters its constitution. Others view the circulatory effects as due primarily to the shift of blood into dilated skin capillaries, that is to a localized hyperemia. This view is particularly advanced in explaining the results of the longer wave-lengths used in heliotherapy. Sonne¹² made determinations of skin and subcutaneous temperatures during irradiation, as a result of which he concluded that the visible and shorter infrared rays produce local temperatures greater than those observed in fevers. His work is of importance in affording some measure of explanation of the differences in the effects produced by sunlight and carbon arc light from those due to the mercury arc which produces less of these rays and more of the short ultraviolet rays.

Another group of German workers regard the effects of general irradiation as due to a generalized protein shock similar to that after the injection of milk or other non-specific proteins. The shock is assumed to result from the introduction into the circulation of the products produced by the destruction of proteins in the cells of the skin. This is particularly adapted to the explanation of the effects following mercury-arc irradiation.

Rothmann¹³ believed the general response due to a lowering of the tone of the sympathetic system.

EFFECTS ON THE SKIN¹⁴

During exposure of the skin to sunlight, an immediate reddening is usually observed. This is a heat erythema due to the longer visible and infrared rays. It is not strictly localized in the irradiated parts and disappears shortly after the irradiation is stopped.

The erythema due to the ultraviolet rays of sunlight is produced only after a latent period of from one to ten hours. It is seen only in the irradiated areas and varies in severity with the intensity and duration of the exposure, blistering accompanying the more intense or longer doses. The erythema persists for several days and is then replaced by an area of pigmentation, the upper epidermal layers scaling off. The pigmentation may persist for several months. These effects were first described in detail by Finsen who employed a carbon arc as the source of light.

During the erythema there is a widening of the capillary blood vessels and at its height, there is leucocytic infiltration and degeneration, particularly of the cells of the Malpighian layer. These later dry to a scale above a regenerated pigmented skin.¹⁵

Ultraviolet radiations are highly absorbed by the skin. Exact measurements of their penetrability are difficult because a portion of the shorter wave-lengths are converted by fluorescence into longer ones in the blue and other portions of the visible region and these have greater penetrability. Vlès and Ugo¹⁶ find the

¹¹ Martini, E., and Roncallo, E., *Boll. soc. ital. biol. sper.*, 11, 77 (1936); *Chem. Abs.*, 30, 6063 (1936).

¹² Sonne, C., *Acta Med. Scand.*, 54, 336 (1921); 56, 619 (1922); *Acta Radiologica Scand.*, 5, 419 (1926); *Chem. Abs.*, 21, 1139 (1927).

¹³ Rothmann, H., *Klin. Wochschr.*, 2, 881 (1923); Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmacol.*, 123, 160 (1927).

¹⁴ Cf. Waller, M. D., *Proc. Roy. Soc.*, 108B, 259 (1931), and for a general discussion, Eidinow, A., *Brit. J. Tuberculosis*, 22, 136 (1928).

¹⁵ For histological details, see Keller, P., *Strahlentherapie*, 16, 52 (1924); 28, 152 (1928); Uhlmann, E., *Ibid.*, 40, 765 (1931). See also Rost, G. A., and Keller, P., in Jadassohn, "Handbuch der Haut und Geschlechtskrankheiten," Vol. 2, Berlin, J. Springer, 1929.

¹⁶ Vlès, F., and Ugo, A., *Compt. rend. soc. biol.*, 123, 226 (1936); *Chem. Abs.*, 31, 713 (1937).

fluorescence spectrum of shaved rat skin to be in part that of the proteins and in part that of cholesterol. Pauli¹⁷ states that the fluorescence curve is to a large extent coincident with the erythema curve. Rabbit skin shows a fluorescence between 5400 and 4200 with a maximum at 5000A. That of human skin has its maximum at 4600A.

Hasselbalch¹⁸ gave the results indicated in Table 24 for the penetration of the rays from a Kromayer water-cooled quartz mercury lamp. Anderson and Macht,¹⁹

Table 24.—Penetration of Rays from Kromayer Lamp.

	Wave Length in Millimicrons						
	436	405	366	354	313	302	297
Per cent transmitted by skin 0.1 mm. thick	59	55	49	42	30	8	2
By skin 1.0 mm. thick	0.5	0.3	0.08	0.02	0.006		

who agreed that dead skin is practically opaque to wave-lengths shorter than 3660A, claimed that live rabbit skin has a much greater transparency, transmitting from 6 to 10 per cent of the energy at wave-lengths between 2537 and 3000A. Bachem and Reed,²⁰ however, were able to find but little difference between live

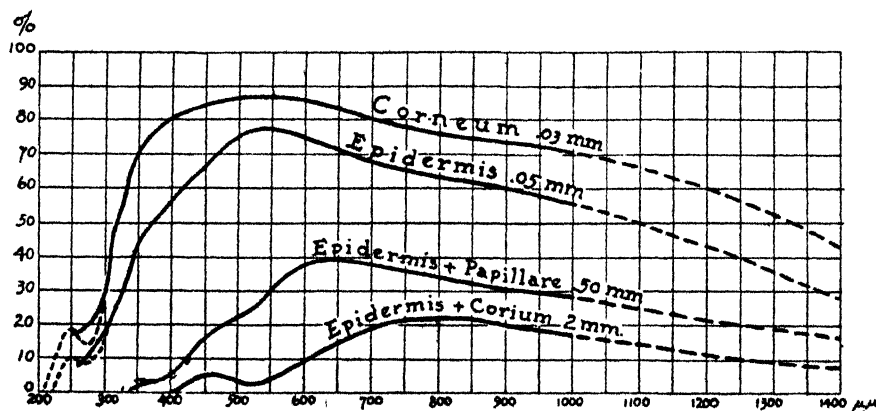


FIGURE 148. Transmission Curves for the Various Skin Layers (Bachem and Reed, *American Journal of Physiology*).

and dead skin if the specimen was kept moist and tightly stretched. They found the wave-lengths of the near infrared and visible regions strongly absorbed by the blood of the corium and subcutaneous layers. The far infrared rays have very little penetrating power and are absorbed in the epidermis. Some of their data are reproduced in Figure 148. The absorption of a band with maximum at 2800A is very great in the corneum and prickle cell layers. On both sides of this band near 3000 and 2500A, the penetration is greater, more radiation reaching the Malpighian layers and the corium.

¹⁷ Pauli, W. E., *Strahlentherapie*, 26, 577 (1927); *Chem. Abs.*, 22, 3672 (1928).

¹⁸ Hasselbalch, K. A., *Skand. Arch. Physiol.*, 25, 55 (1911); *Chem. Abs.*, 5, 2862 (1911).

¹⁹ Anderson, W. T., Jr., and Macht, D. I., *Am. J. Physiol.*, 86, 320 (1928).

²⁰ Bachem, A., and Reed, C. I., *Am. J. Physiol.*, 97, 86 (1931); 90, 600 (1929).

Bachem²¹ has also given data on the ultraviolet transparency of the various layers of the human skin. Figure 149 indicates that the horny layer is very transparent in the visible and near ultraviolet. At 3000A a strong absorption band begins, which has its maximum at 2800A and then diminishes to a minimum at 2600A, increasing again at shorter wave-lengths, and recalling the absorption of

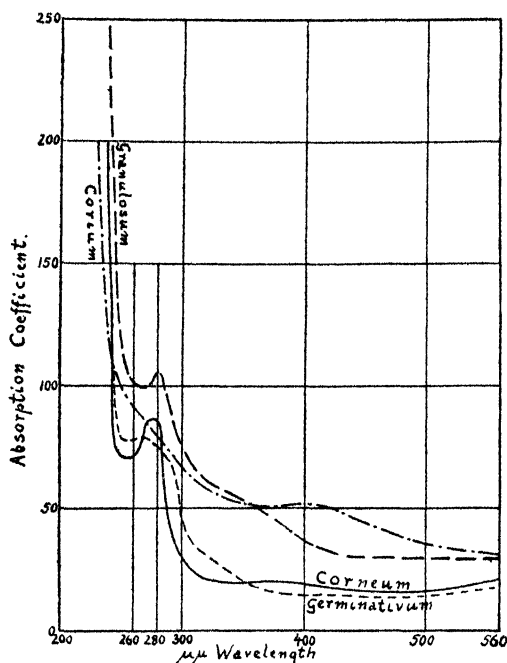


FIGURE 149. Absorption Curves for Various Skin Layers (Bachem, *American Journal of Physiology*).

the proteins. The granulosum layer absorbs somewhat more visible light. Most transparent is the germinating layer. The corium differs in showing the greatest absorption for the visible light. It also shows no absorption maximum at 2800A and has somewhat lower absorption coefficients in the more extreme ultraviolet range. Bachem believes the erythema to originate in the stratum germinativum or corium under the shadow of the upper layers.

Lucas²² has discussed particularly the difficulties involved in this type of measurement. He expressed his results merely in terms of the relation between the logarithms of incident and transmitted light. His observations indicated the skin used to be a hundred to ten thousand times more opaque than that studied by Hasselbalch, much of the loss of radiant energy being due to scattering. In the living animal, however, much of the scattered light may not be lost to the animal. Lucas was unable to detect the passage of any line shorter than 3130A through 0.2 mm. of skin in exposures less than 24 hours. With very thin specimens of epidermis obtained from blisters of the forearm, Lucas obtained the results

²¹ Bachem, A., *Am. J. Physiol.*, **91**, 58 (1929).

²² Lucas, N. S., *Biochem. J.*, **25**, 57 (1931).

of Figure 150, which appear to resemble greatly the curves for the absorption of the amino-acids, tryptophane and tyrosine. These observations appear chiefly of value in demonstrating the extreme difficulty of the problem of measuring the absorption of the skin as a whole, since they had to be limited largely to the epidermis. They do, however, demonstrate that the penetration of ultraviolet rays cannot be more than very slight. Pauli²³ claims that glycerol containing a little alcohol is the best agent for increasing the ultraviolet permeability of the skin.

By the use of a monochromator, Hausser and Vahle²⁴ determined the relative degrees of erythema produced by the various mercury-arc lines, each being adjusted

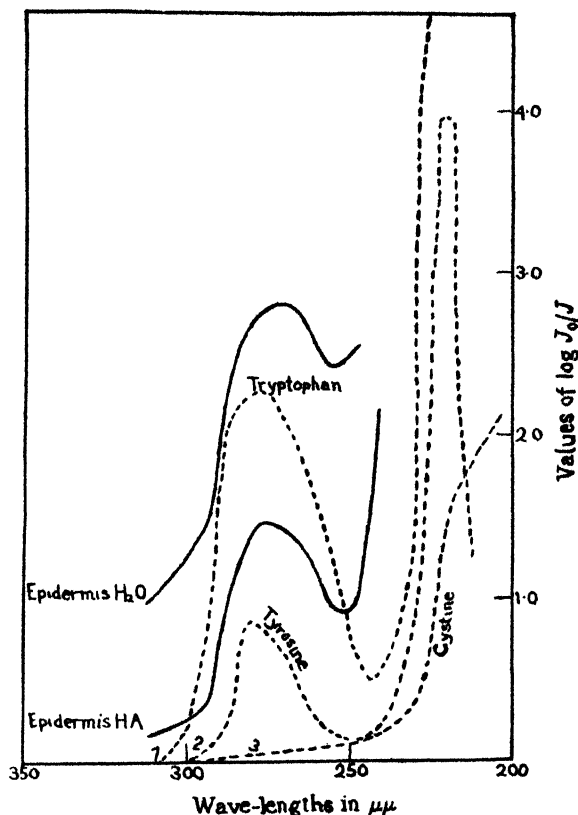


FIGURE 150. Absorption of Skin from a Blister (From Lucas, *Biochemical Journal*).

to the same intensity. They found a maximum sensitivity at 2970Å, the effect beginning at 3130Å. Wave-lengths in the visible and longer ultraviolet had no effect. Adopting the intensity of the erythema produced by the 2970Å line as 100 per cent, the relative values found on irradiation by the other wave-lengths were found to be as indicated in Table 25. In later work, they found a second maximum

²³ Pauli, W. E., *Strahlentherapie*, 26, 577 (1927); *Chem. Abs.*, 22, 3672 (1928).

²⁴ Hausser, K. W., and Vahle, W., *Strahlentherapie*, 13, 41 (1921); 27, 348 (1928); Henri, V., and Moycho, V., [*Compt. rend.*, 158, 1509 (1914)] early placed the maximum irritating effect on rabbit's ear at 2800Å.

Table 25.—Effect of Wave-Length on Erythema.

Wave-Length (A)	Erythema (%)
Greater than 3130	None
3130	4.5
3020	58.
2970	100.
2890	30
2800	28

at 2500A. Luckiesh, Holladay and Taylor,²⁵ using a filter method, confirmed the existence of the maximum at 2970A but found at the shorter wave-lengths values which tended to increase steadily from a minimum at 2800A to 2400A, the shortest wave-length studied. They also studied the reflectance of the skin for various wave-lengths and found it very low for wave-lengths shorter than 3100A. The erythema results of Coblenz, Stair and Hogue²⁶ tended, however, to resemble more closely the values of Hausser and Vahle than those of Luckiesh, Holladay and Taylor at the region near 2540A. Figure 151 compares the results of these workers.

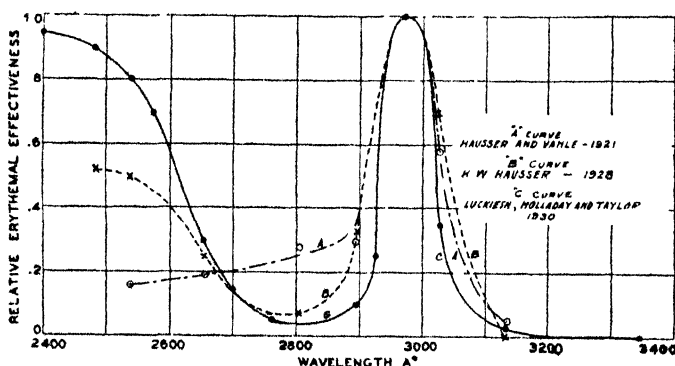


FIGURE 151. Relative Erythema Effectiveness of Equal Amounts of Radiant Energy at Various Wave-lengths. Curve A, according to Hausser and Vahle, 1921; B, according to K. W. Hausser, 1928; C, according to Luckiesh, Holladay and Taylor, 1930. (Luckiesh, Holladay, and Taylor, *Journal Optical Society of America*).

The energy required to produce a minimal perceptible erythema on a sq. cm. of untanned skin by the wave-length 2970A is, according to Coblenz, Stair and Hogue, of the order of 500,000 ergs. There is considerable variation in different persons and in different parts of the body of a given person.²⁷

Luckiesh and Taylor^{27a} find that to produce tanning, exposures to artificial or natural sunlight sufficient to give an appreciable erythema are required. Repeated suberythema doses usually do not tan, although they may be effective in the cure of rickets. With an S-4 sunlamp emitting chiefly narrow bands at 2967, 3022 and 3130A, an exposure of four minutes at a distance of 2.5 feet was

²⁵ Luckiesh, M., Holladay, L. L., and Taylor, A. H., *J. Opt. Soc. Am.*, 20, 423 (1930).

²⁶ Coblenz, W. W., Stair, R., and Hogue, J. M., *Bureau Standards J. Research*, 7, 723 (1931); 8, 541, 759 (1932).

²⁷ See also Adams, E. Q., Barnes, B. T., and Forsythe, W. E., *J. Opt. Soc. Am.*, 21, 207 (1931); Uhlmann, E., *Strahlenherapie*, 35, 361 (1930); Hausser, K. W., and Schlechter, E., *Ibid.*, 27, 348 (1928); Keller, P., *Ibid.*, 34, 129 (1929); 35, 353 (1929).

^{27a} M. Luckiesh and A. H. Taylor, *J. Am. Med. Assoc.*, 112, 2510 (1939).

found necessary to produce on the human arm a minimal perceptible erythema visible one day after the irradiation. To produce a minimal perceptible tanning visible two months later, an exposure of 7.5 minutes was required. These authors also give a curve showing the relative tanning effectiveness of various wave-lengths. It is in general similar to the erythema curve except at the regions on either side of the maximum. Wave-lengths of 2500-2600A are ineffective in tanning, although they may cause a strong erythema. There is some evidence that wave-lengths longer than 3300A may produce immediately after exposure a brownish pigmentation with but little inflammation. This is of little practical significance since the energy densities and times of exposure required are prohibitive.

MECHANISM OF THE PRODUCTION OF ERYTHEMA AND PIGMENTATION

It must be noted that the maximum of erythema production at 2970A corresponds to the absorption maximum of no known cell constituent, notwithstanding the observations of Lucas upon the epidermis alone, in which there was observed a fair degree of similarity to the absorption of proteins. That the wave-length of greatest absorption lies in the region of the least formation of erythema has been interpreted by Hausser and Vahle and by Bachem to indicate that erythema is a process effected in the deeper layers rather than in the epidermis. There is evidence that the erythema produced by wave-lengths of 2500A differs in character from that produced at 2970A in the shade of redness particularly. The reaction to the shorter rays is produced more rapidly and is more transient than that due to the longer ones and, for the same degree of redness, results in less pigmentation, provided the exposure to the short rays is insufficient to produce a severe and lasting burn.

Frankenburger²⁸ noted that the absorption of tryptophane and tyrosine occurs at wave-lengths about 200A on the short wave-length side of the erythema curve. He points out, however, that in alkaline solutions, the absorption of tyrosine at least is shifted to the longer wave-lengths in closer correspondence to the erythema curve. Since this shift is due to salt formation of the phenolic hydroxyl group, it could conceivably also occur when the amino-acid is bound in a protein. For a given incident energy, he calculated the energy effectively absorbed by the tyrosine contained in 80 micra of epidermis beneath 25 micra of corneum and compared it with that of alkaline tyrosine solutions in concentrations roughly equivalent to those in the tissues examined. From the marked similarity of the resulting curves he concluded absorption by tyrosine to be essential to the production of erythema. Although the tyrosine absorbed only from 4 to 13 per cent of the total incident energy at 2970A, it was believed that this was sufficient to produce the erythema. Frankenburger also irradiated 0.4-per cent aqueous solutions of *l*-tyrosine in quartz tubes with unfiltered light from a mercury arc. In air-free water no chemical or spectrographic changes could be detected within six hours. But in the presence of air, the tyrosine quickly changed through a yellow to a deep brown color and carbon dioxide was evolved. Frankenburger believed, as many have, that tyrosine forms first oxindo-compounds and then melanins which are components of the pigment of the skin. During irradiation the absorption increased and extended into the visible region in agreement with the spectra of melanins. Spiegel-Adolf obtains photosynthetic melanins by irradiating tyrosine or tryptophane in alkaline solution or phenylalanine in neutral solution.²⁹

²⁸ Frankenburger, W., *Naturwiss.*, 21, 116 (1933).

²⁹ Spiegel-Adolf, M., *Biochem. J.*, 31, 1303 (1937).

That the process underlying erythema formation is not that of a simple protein coagulation was the conclusion of Clark³⁰ from a comparison of the temperature coefficients of the two types of reaction. That for erythema formation is 2.3 in human and 1.9 in frog skin, but that of the coagulation of proteins (at least in its second stage) is very high, being over ten.

The production of melanin by irradiation of the skin has been effected by Lignac,³¹ but irradiation of four minutes produced the same amount of pigmentation in live skin as several hours of irradiation in dead skin.³² Schmalfuss, Bussmann and Nickelsen³³ believe skin contains other dye-forming substances than tyrosine, capable of darkening without enzymes in light. Intense solar irradiation of a normally pigmented individual causes the appearance of a melanin reaction, the Thormaehlen reaction, in the urine, but this is not observed in the case of previously irradiated and tanned individuals.³⁴

The administration of vitamin C does not affect the pigmentation of human beings following ultraviolet irradiation, according to von Drigalski.³⁵ On the other hand, Schade³⁶ believed the daily administration of this vitamin for ten days after irradiation with an Alpine lamp prevented subsequent pigmentation. Balakhovskii³⁷ claimed the application of carotene in water or dilute alcohol to be beneficial in curing ultraviolet burns.

Lewis has long considered histamine or histamine-like substances of importance in the production of erythema, whether by irradiation or by heat, mechanical or electrical causes.³⁸ The mechanism of their liberation by irradiation does not appear to be a nervous one, since erythema may be produced after the nerves supplying the skin have been cut. Novocaine injected intradermally does lessen erythema formation, but this may be due to an internal filtering action. Krogh³⁹ believes that, although histamine may be formed, the predominant dilating compound in ultraviolet erythema must be a material of extremely low diffusibility. Otherwise it would diffuse into the blood through the enormous surface of the dilated blood vessels and thus be lost.

In a preceding chapter, mention was made of the belief of Ellinger that histamine may be photochemically produced by the decarboxylation of histidine. Frankenburg, however, pointed out that the absorption of histidine is great only at wave-lengths too short to permit the erythema curve to be accounted for by a direct action on histidine. He did, however, suggest that when this amino-acid is bound in peptide linkages, its absorption spectrum might be sufficiently displaced toward the longer wave-lengths to permit some absorption and photochemical change. He also described the production of a new absorption band at 3150 to 3200A during the irradiation of histidine solutions in the absence of oxygen. This new absorption did not resemble that of histamine, and histamine itself when irradiated also exhibited a new type of longer wave-length absorption. From his

³⁰ Clark, J., *Am. J. Hyg.*, **24**, 334 (1936).

³¹ Lignac, G., *Nederland Maanschr. Genesck.*, **16**, 496 (1930); *Chem. Abs.*, **24**, 1873 (1930).

³² See also Lovisatti, N., [*Forsch. Geb. Röntgenstrahlen*, **44**, 235 (1931); *Chem. Abs.*, **25**, 5679 (1931)] for the function of the melanotic pigments in increasing the ultraviolet tolerance.

³³ Schmalfuss, H., Bussmann, G., and Nickelsen, O., *Arch. Dermatol. Syphil.*, **175**, 39 (1937); *Chem. Abs.*, **31**, 5422 (1937).

³⁴ Risak, E., and Asperger, H., *Klin. Wochschr.*, **11**, 154 (1932); *Chem. Abs.*, **26**, 3553 (1932).

³⁵ von Drigalski, W., *Klin. Wochschr.*, **13**, 1374 (1934); *Chem. Abs.*, **29**, 1138 (1935); Tenchio, F., *Klin. Woch.*, **13**, 1511 (1934); *Chem. Abs.*, **29**, 1139 (1935).

³⁶ Schade, H., *Klin. Woch.*, **14**, 60 (1935); *Chem. Abs.*, **29**, 4045 (1935).

³⁷ Balakhovskii, S., *Compt. rend. acad. sci. U.R.S.S.*, **1**, 28 (1934); *Chem. Abs.*, **28**, 2736 (1934).

³⁸ Lewis, T., "The Blood Vessels of the Human Skin and Their Responses," London, Shaw and Sons, 1927.

³⁹ Krogh, A., "The Anatomy and Physiology of the Capillaries," New Haven, Yale University Press, 1929.

observations it would appear that in irradiated histidine solutions, histamine could at best be present in very slight concentrations, probably insufficient to account for the vasodilatation of erythema. Ellinger⁴⁰ found no difference in effects on the blood pressure of the cat or on the surviving guinea pig intestine of extracts prepared from skin before and after ultraviolet irradiation. Frankenburg concludes that the erythema reaction is a complex one, since strong erythema can be produced in the range of wave-lengths (3100 to 2750A) which fail to affect histidine. Accordingly, if histamine or some other erythema-producing substance is formed it must be indirectly produced. He also suggested that the changes induced in tyrosine are accompanied by changes in the protein of which it forms a part and that these are of a nature which increases the permeability of the membranes releasing substances of histamine-like nature normally present in cells.

Various workers have attempted to correlate the temperature of the skin when irradiated with the severity of the effects produced. Thus, Shattock and Waller⁴¹ believe that if the tissues are heated simultaneously with or shortly after exposure, the erythema is delayed or suppressed. On the other hand, exposure to heat before the irradiation increases the erythema produced. Hill⁴² and Eidinow also believed that hyperemia tends to increase the effects of irradiations with the quartz lamp. Schall and Alius,⁴³ and Cramer and Fechner,⁴⁴ however, found little if any such effect.

Lehner and Urban⁴⁵ observed that repeated exposure of a definite area of normal skin produced after the first few treatments a more prompt and intense reaction, but after about three treatments there was little itching and scarcely any hyperemia. At the same time the spot so treated became less sensitive to other irritants, such as the injection of morphine. Ten minutes after the exposure of the entire back to the lamp, the skin of the breast or upper arm was more sensitive than normally to the injection intracutaneously of morphine solutions, but this hypersensitivity persisted for only thirty minutes. It has been stated that by giving repeated doses the skin may be induced to develop a tolerance to ultraviolet light so that the sensitivity may be reduced to as low as 8 per cent of its normal value for the individual. The filtering action of the pigments produced may play some part in this acquired tolerance, but other factors are probably concerned. Relatively little is known exactly about the production of tolerance. Antibodies do not seem to be concerned.

Sensitization of the skin has been observed. After rats have been injected intraperitoneally with chlorophyll, the erythema and hyperemia produced on irradiation of a portion of the skin were much more pronounced than in uninjected animals, according to Fulchignoni.⁴⁶ There has also been reported a case in which an alcoholic solution of chlorophyll when rubbed on the skin penetrated to the deeper layers and sensitized it so that a short exposure of the treated part to red or to ultraviolet light produced erythema, although the surrounding untreated parts were unaffected.⁴⁷ Proft⁴⁸ found some soaps to increase the erythema due to light. This he believed to be independent of the presence of a sensitizing dye such as chlorophyll or the pigment of linseed oil, and also independent of the horny epithelium. Instead, he believed it due to the presence of free alkali. A weakened erythema results from the use of oils, fats and undissolved soaps and absolute protection was afforded by a 10-per cent alcoholic salicylic acid solution. The pH of the skin alters its light sensitivity, according to Marchionini and Hövelborn,⁴⁹ who found that pretreatment with a salve of pH 2.7 increased its sensitivity. Skin treated with an alkaline salve required two and a half

⁴⁰ Ellinger, F., *Arch. Exp. Path. Pharmacol.*, **149**, 343 (1930).

⁴¹ Shattock, F., and Waller, M. D., *Lancet*, **II**, 917 (1929).

⁴² Hill, L., and Eidinow, A., *Lancet*, **II**, 299 (1924); see also Török, L., Lehner, E., and Urban, F., *Krankheitsforsch.*, **5**, 293 (1927); *Chem. Abs.*, **22**, 4167 (1928).

⁴³ Schall, L., and Alius, H. J., *Strahlentherapie*, **26**, 649 (1927); **27**, 769 (1927-8).

⁴⁴ Cramer, H., and Fechner, G., *Ibid.*, **39**, 474 (1931).

⁴⁵ Lehner, E., and Urban, F., *Krankheitsforsch.*, **4**, 381 (1927); *Chem. Abs.*, **22**, 4166 (1928).

⁴⁶ Fulchignoni, F., *Boll. soc. ital. biol. sper.*, **11**, 428 (1936); *Chem. Abs.*, **31**, 1053 (1937).

⁴⁷ Kitchavatz, M., *Compt. rend. soc. biol.*, **116**, 675 (1934); *Chem. Abs.*, **28**, 5839 (1934); *Ann. de Dermat. et Syph.*, **5**, 293 (1934).

⁴⁸ Proft, H., *Strahlentherapie*, **40**, 351 (1931); *Chem. Abs.*, **25**, 3675 (1931).

⁴⁹ Marchionini, A., and Hövelborn, C., *Arch. Dermatol. Syphilis*, **174**, 251 (1936); *Chem. Abs.*, **30**, 7591 (1936).

times as much exposure as the acid-treated skin to produce an erythema. Papcke⁸⁰ believes peroral administration of an isotonic mixture of calcium, potassium and magnesium salts to decrease the erythemic response.

Irradiation of the skin of the guinea pig previously injected with methylene blue decolorizes it irreversibly. The skin of the frog similarly colored is decolorized in darkness but the color is restored on irradiation.⁸¹ Wohlgenuth and Sugihara⁸² found suitable irradiation of a guinea pig with natural or artificial sunlight to cause in the skin an increase of the enzyme phenolase, some decrease in lipase and a notable decrease in diastase. The blood enzymes were not affected. Other workers have shown therapeutic doses of ultraviolet light to affect the intracellular oxidase, peroxidase and catalase of the skin. Natural sunlight injures somewhat the ability of the skin to produce lactic acid, but artificial sunlight is more injurious and x-rays even more so.⁸³ Harpuder⁸⁴ found irradiation of the skin up to beginning erythema to affect the diffusion of chloride, calcium and potassium ions. Changes in the contents of water, sodium, potassium and calcium in the pigmented skin of rabbits after its irradiation by ultraviolet rays proceed in the same direction and reach the same values as in unpigmented skin.⁸⁵ The contents of sugar and glycogen in pigmented skin are less than in unpigmented skin, but the changes on irradiation proceed alike. No habituation could be observed in the changes in mineral and carbohydrate metabolism of the skin after irradiation.

Skin irradiated with ultraviolet light shows an increase in cholesterol content of from 7 to 150 per cent, according to Roffo.⁸⁶ The skin from various parts of the face contains from two to seven times as much cholesterol as skin from the abdomens of the same persons, and the distribution in the face is roughly proportional to the amount of exposure to the sun. Roffo also believed that there was a direct relationship between the frequency of skin tumors and the proportion of cholesterol in the skin. If white rats are kept in darkness there is a lowering of the cholesterol content of the skin.⁸⁷ These results were confirmed by Kawaguchi.⁸⁸

Loewy and Cronheim⁸⁹ find that the non-protein nitrogen of rat or guinea-pig skin is not affected by five hours of irradiation. The chlorine content decreased either in darkness or under ultraviolet irradiation. Potassium was lowered by irradiation and unaffected by darkness in the rat but increased in guinea-pig skin. Magnesium was increased by irradiation but the calcium content was not altered. Beck⁹⁰ claimed local applications of a Vitrisol preparation made by prolonged irradiation of spinach gave good results in the treatment of acne vulgaris and lupus vulgaris. In the repair of cutaneous lesions, cholesterol has the greatest healing action, followed by irradiated ergosterol and then ergosterol.⁹¹ It has been stated that in scleroderma, treatment with massive doses of the vitamin reduces the abnormal calcium deposits from the skin before that element is removed from the bones.⁹² The antigen-antibody reaction in skin is inhibited by ultraviolet irradiation, according to Albus and Feldermann.⁹³ The total

⁸⁰ Papcke, G., *Arch. Dermatol. Syphilis*, 168, 476 (1933); *Chem. Abs.*, 28, 525 (1934).

⁸¹ Dubouloz, P., and Rochette, J., *Compt. rend. soc. biol.*, 122, 221 (1936); *Chem. Abs.*, 31, 3069 (1937).

⁸² Wohlgenuth, J., and Sugihara, N., *Biochem. Z.*, 163, 260 (1925).

⁸³ Wohlgenuth, J., and Ikebaki, T., *Biochem. Z.*, 186, 43 (1927); *Chem. Abs.*, 21, 3632 (1927).

⁸⁴ Harpuder, K., *Z. ges. Exptl. Med.*, 76, 724 (1931); *Chem. Abs.*, 26, 4834 (1932).

⁸⁵ Kaplanskif, S. Y., and Kaplanskaya-Raiskaiya, S. I., *Arch. sci. biol. (U.S.S.R.)*, 39, 169, 175 (1935); *Chem. Abs.*, 30, 7185 (1936).

⁸⁶ Roffo, A. E., *Bol. inst. med. exptl. estudio cancer*, No. 39, 358, 390 (1935); Roffo, A. H., Jr., *Ibid.*, 41, 41 (1936); *Chem. Abs.*, 31, 4347 (1937); *Bol. inst. Med. Exptl.*, 6, 370 (1929); *Chem. Abs.*, 26, 1304 (1932); *Compt. rend.*, 201, 566 (1935).

⁸⁷ Roffo, A. H., *J. Physiol. Path. Gén.*, 29, 739 (1931); *Chem. Abs.*, 26, 2993 (1932); *J. physiol. Path. Gén.*, 30, 345 (1932); *Chem. Abs.*, 26, 5330 (1932); *Bol. inst. med. exptl.*, 8, 32 (1931); *Chem. Abs.*, 29, 5871 (1935); *Arch. elect. med.*, 42, 425 (1934); *Chem. Abs.*, 31, 6682 (1937); Roffo, A. E., Jr., *Bol. inst. med. exptl. estudio cancer*, 14, 447 (1937); *Chem. Abs.*, 32, 3812 (1938).

⁸⁸ Kawaguchi, S., *J. Biochem. Japan*, 15, 111 (1932); *Chem. Abs.*, 26, 2995 (1932); see also Chorzak, T., *J. Physiol. Path. Gén.*, 31, 408 (1933); *Chem. Abs.*, 28, 3473 (1934).

⁸⁹ Loewy, A., and Cronheim, G., *Biochem. Z.*, 256, 411 (1932).

⁹⁰ Beck, H., *Munch. med. Wochschr.*, 74, 1129; *Chem. Abs.*, 22, 4655 (1928). For the use of Viosterol in acne, see Doktorsky, A., and Platt, S. S., *J. Am. Med. Assoc.*, 101, 275 (1933).

⁹¹ Tautini, E., *Sperimentale*, 89, 712 (1935); *Chem. Abs.*, 30, 7696 (1936); see Kemmler, H., *Mitt. Grenz. Med. Chir.*, 43, 453 (1934); *Chem. Abs.*, 29, 5927 (1935).

⁹² Cornbleet, T., and Struck, H. C., *Arch. Dermatol. Syphilol.*, 35, 188 (1937); *Chem. Abs.*, 31, 1487 (1937).

⁹³ Albus, G., and Feldermann, F., *Klin. Wochschr.*, 17, 1702 (1938); *Chem. Abs.*, 32, 6677 (1938).

glutathione of rabbit skin appears to be increased following irradiation, probably because of a disintegration of tissue proteins.⁶⁴

Sunburn Creams and Protective Salves. A great number of skin creams for the prevention of sunburn are on the market and some contain materials which simulate a tan.⁶⁵ Malowan⁶⁶ states that the ointments which protect fluoresce strongly in ultraviolet light. Prominent constituents are naphtholsulfonic acid, and esculin and its homologs. Eder and Freund⁶⁷ propose salves or emulsions containing in addition to esculin or naphtholsulfonic acid, lithopone or a compound of titanium. Dunning⁶⁸ suggested the use of the sodium salt of a mono- or di-sulfonic acid of *o*- or *p*-hydroxybiphenyl. Hall⁶⁹ employs a polyhydric alcoholic ester of salicylic acid, such as glycerol or glycol mono-salicylate with a mineral oil, or with stearic acid, lanolin, beeswax, etc. Stockelbach⁷⁰ employs menthyl salicylate in a vehicle of alcohol, an oil or a cosmetic cream for preventing sunburn. Risler⁷¹ mixed a phosphorescent zinc sulfide with about six times as much of a cream phase made by heating and mixing together stearic acid 170, glycerol 210, water 569, and 10-per cent aqueous ammonia, 50. When cold, one part of violet essence was added.

The I. G. Farbenindustrie⁷² proposed such substances as aryl benzimidazoles or aryl benzothiazoles. Issermann, Ohlsson and Orelup propose about 0.5 to 1 per cent of an amino- or substituted amino-benzoic acid, as benzylamino-*o*-benzoic acid, in peanut or almond and mineral oils.⁷³ Jordan suggests dibenzalacetone as an effective component.⁷⁴

In the past, quinine bisulfate was frequently employed in salves to act as an internal filter.⁷⁵ Other materials specified in the I. G. Farbenindustrie patents included stilbene, 2-phenylindole, α -phenylcinnamionitrile, 2-phenylquinoline, N-acetyl-carbazole, μ -methylnaphthoxazole and 2-acetyl-3-bromoindazole. Schwarz suggests a cream containing oak bark extract.⁷⁶ Sodium phenylbenzimidazolesulfonate or other substances with sharp absorption of wave-lengths in the range 3200 to 3500A are claimed by Merkel and Wiegand to absorb noxious rays without excluding tanning rays.⁷⁷

It has been claimed that sunburn does not follow exposure after vitamin C has been given intravenously and bergamot oil has been applied to the skin.⁷⁸

⁶⁴ Matusis, I. I., and Grechanovskii, *Bull. biol. med. exptl. U.R.S.S.*, 3, 489 (1937); *Chem. Abs.*, 32, 8449 (1938).

⁶⁵ For general discussions see: Lendle, A., *Pharm. Ztg.*, 81, 903 (1936); Stambovsky, L., *Drug and Cosmetic Ind.*, 36, 551, 554 (1935); Van Itallie, P. H., *Drug Trade News*, 12, No. 8, 41, 44, 45, 47 (1937); Augustine, J., *Riechstoff Ind. Kosmetik*, 11, 218 (1936); Karl, P., *Ibid.*, 12, 92 (1937); Goodman, H., *Ann. Perfumer*, 34, No. 6, 47 (1937); Böhme, H., and Reichert, B., *Arch. Pharm.*, 275, 437 (1937); Kalisch, J., *Drug Cosmetic Ind.*, 42, 52 (1938); Heber, C. F., *Svensk Kem. Tids.*, 50, 144 (1938); Calame, A., *Seifensieder-Ztg.*, 65, 456 (1938); Gattefossé, *Parfumerie moderne*, 32, 97, 113 (1938).

⁶⁶ Malowan, L. S., *Seifensieder-Ztg.*, 61, 335, 353 (1934); *Chem. Abs.*, 28, 4836 (1934).

⁶⁷ Eder, J. M., and Freund, L., *Austrian P.* 138,527, Aug. 10, 1934; *Chem. Abs.*, 29, 558 (1935).

⁶⁸ Dunning, F., U. S. P. 2,015,005, Sept. 17, 1935; *Chem. Abs.*, 29, 7587 (1935).

⁶⁹ Hall, R. A., U. S. P. 2,081,117, May 18, 1937, to Colgate-Palmolive-Peet Co.; *Chem. Abs.*, 31, 5111 (1937).

⁷⁰ Stockelbach, F. E., U. S. P. 2,041,874, May 26, 1936; *Chem. Abs.*, 30, 5000 (1936).

⁷¹ Risler, J., U. S. P. 1,779,891, Oct. 28, 1930; *Chem. Abs.*, 25, 174 (1931).

⁷² French P. 770,912, Sept. 24, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 29, 892 (1935); *British P.* 435,811, Sept. 30, 1935.

⁷³ Issermann, S., Ohlsson, E., and Orelup, J. W., U. S. P. 2,102,712, Dec. 21, 1937; *Chem. Abs.*, 32, 1410 (1938).

⁷⁴ Jordan, A., German P. 652,929, Nov. 10, 1937; *Chem. Abs.*, 31, 1410 (1938).

⁷⁵ See Hazen, H. H., *Am. J. Nursing*, 38, 791 (1938).

⁷⁶ Schwarz, H., *Seifensieder-Ztg.*, 64, 518 (1937); *Chem. Abs.*, 31, 6413 (1937).

⁷⁷ Merkel, E., and Wiegand, C., U. S. P. 2,104,492, Jan. 4, 1938; *Chem. Abs.*, 32, 1869 (1938).

⁷⁸ Urbach, E., and Kral, F., *Klin. Wochschr.*, 16, 960 (1937); *Chem. Abs.*, 31, 8015 (1937).

Secerov⁷⁹ found that after five to forty hours of exposure to ultraviolet rays the hair of a white guinea pig became yellow. In rats the production of alopecia by thallium is said to be reduced or retarded by the action of ultraviolet rays, which also accelerate the regeneration of hair in the bald spot.⁸⁰

Light may be concerned in the production of argyria, the deposition of silver in the skin, after internal administration of silver salts.⁸¹ The same may also be true of chrysiasis, the deposition of gold, after prolonged treatment with the gold compound, Sanocrysin.⁸²

METABOLISM AND CIRCULATION

Only after very intense irradiation is the general body temperature elevated. When a sufficient amount of tissue damage has been done there may be a fever similar to that which follows the injection of protein destruction products. The effects of irradiation upon the basal metabolism are of little importance. During irradiation it may be increased by as much as 18 per cent, but it quickly returns to normal on the cessation of irradiation and remains unchanged during the erythema state.⁸³ Harris⁸⁴ found that ultraviolet radiation exerts a stimulant action on the gaseous metabolism of small animals and on the movements of the isolated stomach of the frog. This stimulus he believed to be completely annulled by visible radiation, the antagonism being physiological rather than physical. He also stated that exposure of an animal to the mixed radiations of a powerful source of light depresses its heat production, the depression being greater in pigmented animals than in albinos.

No effect on the basal metabolism of healthy men, mice or rats could be observed by Campbell⁸⁵ on exposure to a mercury-vapor lamp, or to its rays when filtered through Uviol glass, or to visible light. On the other hand, Sonne⁸⁶ found that the oxygen consumption of the chrysalids of the meal worm could be accelerated by light energy of from 1 to 200 gm. cal. per minute per sq. cm. The shorter wave-lengths had the greater effect. There was an increase of about 40 per cent during an exposure of 45 minutes to the unfiltered light of a Kromayer lamp, of about 20 per cent when a glass filter was used and of about 10 per cent when both a glass filter and a methylene blue filter were used. Yellow light had no influence on the respiratory metabolism. An increase of about 15 per cent persisted for several hours after irradiation by unfiltered light, but there were no after effects following irradiation by filtered light which eliminated the central band of ultraviolet frequencies.

Crofts⁸⁷ observed a 14-per cent fall in oxygen consumption in canaries on ultraviolet irradiation. This was followed two to six days after the exposure by a rise of 21 per cent. In normal rabbits and in six normal human subjects, no effects were noted which could be ascribed to the irradiation. Lippmann and Völker⁸⁸ found a slight increase in human subjects (10 to 18 per cent) but the metabolism

⁷⁹ Secerov, S., *Compt. rend.*, **158**, 1826 (1914).

⁸⁰ Buschke, A., and Vasarhelyi, J., *Klin. Wochschr.*, **11**, 678 (1932); *Chem. Abs.*, **27**, 779 (1933).

⁸¹ Lenartowicz, J., and Jalowy, B., *Arch. Dermatol. Syphilol.*, **9**, 483 (1938); *Chem. Abs.*, **32**, 9266 (1938).

⁸² Schneidewind, A., Albertal, M., and Trajtenberg, S., *Rev. asoc. med. argentina*, **52**, 792 (1938); *Chem. Abs.*, **32**, 9264 (1938).

⁸³ See, however, Kestner, O., Peemöller, F., and Plaut, R., [*Klin. Wochschr.*, **2**, 2108 (1923)], Kestner, O., Peemöller, F., and Schadow, H., [*Pflüger's Arch. ges. Physiol.*, **217**, 473 (1927)], and Kestner, O., and Schadow, H., [*Ibid.*, **217**, 492 (1927)] for a different point of view.

⁸⁴ Harris, D. T., *Proc. Roy. Soc.*, **96B**, 171 (1925).

⁸⁵ Campbell, J. A., *Proc. Roy. Soc.*, **99B**, 451 (1926).

⁸⁶ Sonne, C., *Acta Radiol. Skand.*, **5**, 419 (1926); *Chem. Abs.*, **21**, 1139 (1927).

returned to normal shortly after the irradiation was discontinued. The administration of iodine did not increase nor prolong the effect. Mělka⁸⁹ found a 14- to 47-per cent increase in oxygen consumption in persons exposed to the noon July sun. It has been stated⁹⁰ that in certain persons the quartz mercury lamp may produce a fall in total metabolism. This is the effect when the blood bilirubin is high, or if the skin is abundantly pigmented or if there has been an excessive consumption of buckwheat. The effect is ascribed to photosensitization.⁹¹

Pincussen⁹² found solar irradiation to stimulate the protein metabolism of rabbits as shown by an increased nitrogenous excretion. This was still further increased by sensitizers such as dyestuffs and potassium iodide. Liebesny⁹³ fed two dogs on a constant diet of horse tripe and found exposure to the ultraviolet rays from a mercury-vapor lamp to cause an appreciable reduction in the volume of urine and in the total nitrogen, creatinine, and neutral sulfur content. Yoshine⁹⁴ observed a slight rise in the positive nitrogen balance of irradiated dogs if the exposure was short, but this changed to a negative balance when longer exposures were given. Longer periods of irradiation led to disturbances in the absorption of nitrogenous substances in the intestine and to a refusal of food. The slight irradiation which caused the positive balance consisted of a one-hour irradiation on each of eight consecutive days. The severe irradiation consisted of four hours of exposure daily. Fontès and Yovanovitch⁹⁵ believed that the exclusion of light decreases the nitrogen metabolism nearly to the level attained during sleep, and that the decrease during sleep while exposed to light is less than that in sleep in darkness. On the other hand, Mayerson, Gunther and Laurens⁹⁶ found that in adult dogs transient increases in the endogenous nitrogen metabolism, and in the absorption of calcium and phosphorus from the intestine, resulted when the animals were taken from light to darkness or *vice versa*. It was concluded that any deviation from the usual supply of radiant energy acts as a transient stimulus to these metabolic processes.

Exposure of normal men, women and children to summer sunlight or to a carbon arc causes an increase in creatinine excretion during the period of irradiation, according to Eichelberger,⁹⁷ but for a few hours subsequently there is a decreased excretion. No effect was observed on the excretion of creatine or on the basal metabolic rate.

Nothhaas and Schadow⁹⁸ studied the nitrogen balance of a series of children, first in Hamburg and again at the sea-shore. In spite of inadequate diet, nitrogen retention is increased under the latter conditions, even although the weight may not be increased. Other children remaining in Hamburg and treated with artificial ultraviolet light showed irregular effects, but in some a positive nitrogen balance was obtained.

⁸⁷ Crofts, E., *Am. J. Hygiene*, **8**, 1014, 1024 (1928); *Chem. Abs.*, **23**, 2466 (1929).

⁸⁸ Lippmann, A., and Völker, H., *Klin. Wochschr.*, **7**, 213 (1928); *Chem. Abs.*, **22**, 1168 (1928).

⁸⁹ Mělka, J., *Bratislava Lekárske Listy*, **6**, 50 (1926); *Chem. Abs.*, **22**, 4137 (1928).

⁹⁰ Mason, D. H., and Mason, H. H., *Arch. Int. Med.*, **39**, 317 (1927); *Chem. Abs.*, **21**, 2303 (1927).

⁹¹ Summarizing lectures on the effect of light on metabolism have been given by Pincussen, L., *Strahlentherapie*, **48**, 308 (1933) and by Mangold, E., *Ibid.*, **319**.

⁹² Pincussen, L., *Biochem. Z.*, **150**, 36 (1924).

⁹³ Liebesny, P., *Z. Physik. Diätet. Therap.*, **24**, 182 (1920); *Chem. Abs.*, **15**, 2905 (1921).

⁹⁴ Yoshine, S., *Strahlentherapie*, **18**, 201 (1924); *Chem. Abs.*, **20**, 1430 (1926).

⁹⁵ Fontès, G., and Yovanovitch, A., *Compt. rend. soc. biol.*, **93**, 269 (1925); *Chem. Abs.*, **19**, 3527 (1925).

⁹⁶ Mayerson, H. S., Gunther, L., and Laurens, H., *Am. J. Physiol.*, **75**, 399, 421 (1926).

⁹⁷ Eichelberger, M., *J. Biol. Chem.*, **69**, 17 (1926).

⁹⁸ Nothhaas, R., and Schadow, H., *Jahrb. Kinderheilk.*, **127**, 1 (1930); *Chem. Abs.*, **26**, 763 (1932); see also Ferri, U., *Pediatrics Rev.*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).

Pincussen, Bayerl, Brück, Görne and Rothmann,⁹⁹ believed irradiation of pigs with infrared, visible and ultraviolet light to cause, in general, increased elimination of total nitrogen and of purines.

The discrepancies in these reports are due, in part, to the differences in the subjects and the nature and duration of the exposures, and in part to the time following irradiation when the observations were made. It is apparent that no very marked changes occur in most individuals. Lehmann and Szakáll¹⁰⁰ found the effect of ultraviolet irradiation at weekly intervals lowered the basal metabolism of six human subjects 10 to 15 per cent, and increased the capacity for work up to 60 per cent, while decreasing the oxygen debt. The various effects were believed to be very similar to the results attained by training. When an ultraviolet-impervious screen was interposed without the knowledge of the subject, the increased capacity for work did not occur. Another subject showed a loss of weight, a lowering of the basal metabolism and a rise in the respiratory quotient when treated, in contrast to a daily fall in weight and a slight increase in the alkali reserve when not treated.

The pulse rate is usually unaltered, and circulatory effects are not prolonged. The blood pressure is usually lowered, but the circulatory changes are not remarkable. As early as 1905, Hasselbalch¹⁰¹ observed decreases of from 8 to 10 per cent in blood pressure which lasted for several months following the application of massive doses of the rays from a carbon arc. He ascribed the effects to the cutaneous hyperemia. The most thorough recent studies are by Laurens and Mayerson.¹⁰²

Reed¹⁰³ showed that irradiation of the eyes of anesthetized dogs caused a considerable drop in the arterial blood pressure, but there was no evidence for the liberation of a depressor substance into the blood. The effect could not be ascribed solely to nervous factors since it was not abolished by bilateral section of the vagi and section of the optic nerve. The effect was attributed to a direct action upon the blood, since similar effects resulted from the irradiation of the blood circulating through a quartz tube interposed in the carotid artery. The light used was that of a carbon arc and the results were the same when either the infrared rays or the ultraviolet rays of wave-lengths shorter than 3300A had been removed. The coagulation time of the blood was increased, and it was necessary to use intravenous injections of heparin to prevent coagulation of the blood in the circulation. There were no marked effects upon the hemoglobin content or upon the red blood cells, but the white cells decreased, with a relative lymphocytosis and an absolute lymphopenia.¹⁰⁴

Rowinski¹⁰⁵ could detect no change in the vasoconstricting power of the blood serum of patients who had taken sea or sun baths. Sidoli¹⁰⁶ found that irradiation of the blood serum *in vitro* caused a decrease in its power of vasoconstriction proportional to the intensity of the radiation employed. This he ascribed to a

⁹⁹ Pincussen, L., Bayerl, V., Brück, E., Görne, J., and Rothmann, A., *Strahlentherapie*, 45, 401 (1932); *Chem. Abs.*, 27, 4836 (1933).

¹⁰⁰ Lehmann, G., and Szakáll, A., *Arbeits. Physiol.*, 5, 278 (1932); 6, 84 (1932); *Chem. Abs.*, 28, 2396 (1934).

¹⁰¹ Hasselbalch, K. A., *Skand. Arch. Physiol.*, 17, 431 (1905); *Berlin Klin. Wochschr.*, 44, 1247 (1907).

¹⁰² Laurens, H., and Mayerson, H. S., *Am. J. Physiol.*, 84, 524 (1928).

¹⁰³ Reed, C. I., *Am. J. Physiol.*, 74, 511, 518, 525 (1925); bibliography of effect of light on blood pressure is included.

¹⁰⁴ Reed, C. I., *Archiv. Phys. Ther. X-Ray, Radium*, 8, 108 (1927).

¹⁰⁵ Rowinski, P., *Boll. soc. ital. biol. sper.*, 6, 818 (1931); *Chem. Abs.*, 26, 1966 (1932).

¹⁰⁶ Sidoli, E., *Arch. sci. biol. ital.*, 19, 443 (1934); *Chem. Abs.*, 29, 3359 (1935).

decrease of the adrenalin present in the serum. During irradiation *in vivo*, however, there is no such change.¹⁰⁷

EFFECTS ON THE BLOOD

The effect of a general irradiation of the body upon the formed elements of the blood is not remarkable, at least in normal individuals. The literature is extensive but frequently contradictory. To summarize the individual papers would leave the reader with a feeling of confusion, and would consume much space. Instead, only a few of the more significant conclusions which it seems possible to draw will be stated, together with references to a few papers from which, as well as from the special works cited earlier in the chapter, the reader may obtain more complete references to other work.¹⁰⁸

Several writers have found no changes induced in the cell count by irradiation.¹⁰⁹ It seems to be established that normal men or other animals can live on an ample balanced diet for prolonged periods during which sunlight or artificial illumination is absent or much reduced without the production of an anemia.

Hardy¹¹⁰ tabulated the data of some 45 investigators. Eleven reported no change in the red cells, while 18 reported an increase and only two a decrease. There were wide differences in the species of animal used, and in the conditions of irradiation, sources, energies and wave-lengths. Her own conclusions, after a careful weighing of the available evidence, were that a normal red cell count may be very slightly increased and a low one raised to normal by daily irradiations. Most observers have reported a leucocytosis after ultraviolet irradiation, but there is much variation both in the amount of change in the total white cell count and in the differential count.

One reason for the variations in the results of different observers is that, as pointed out by Balderrey and Barkus,¹¹¹ the primary effect of irradiation is a vasodilatation followed by a diffusion of tissue fluid into the blood stream, resulting in dilution and increased blood volume. When the irradiation is long-continued or frequently repeated, this effect may be counteracted by vasoconstriction and blood concentration. Thus, alterations in blood concentration may tend to mask any real variations in the numbers of the various formed elements. At different periods during and after irradiation, these opposing effects may predominate to varying degrees and cause confusion. Mayerson and Laurens¹¹² found a single exposure to carbon arc radiations to produce a temporary increase in the plasma volume of the blood of dogs, amounting to 6 to 37 per cent, and followed by recovery to normal within five hours. Repeated exposures caused an increase in the number of red cells of 10 to 19 per cent, maintained for three to six weeks after the final irradiations. The color, volume and saturation indexes showed that the cells in the post-irradiation period were usually smaller and less saturated than before irradiation. The platelets dropped in number and volume by 35 per

¹⁰⁷ See also Johnson, J. R., Pollock, B. E., Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, 114, 594 (1936).

¹⁰⁸ For a review, see Furniss, A., *Brit. J. Actinother.*, 5, 187 (1930); an alteration in the absorption spectrum of hemolyzed blood was not found following irradiation of the subject by Varshaver, G. S., *Arch. sci. biol. (U.S.S.R.)*, 41, No. 2, 31 (1936); *Chem. Abs.*, 31, 7905 (1937).

¹⁰⁹ Jaulmes, C., *Compt. rend. soc. biol.*, 92, 268 (1925); Koopman, J., *Deut. med. Wochschr.*, 50, 277 (1924); *Chem. Abs.*, 18, 2197 (1924); Tataranu, I., *Compt. rend. soc. biol.*, 97, 1736 (1927); *Chem. Abs.*, 22, 1799 (1928); Sinclair, R. D., *Sci. Agr.*, 13, 737 (1933) (in pigs); *Chem. Abs.*, 23, 3955 (1929).

¹¹⁰ Hardy, M., *Am. J. Hygiene*, 7, 811 (1927); 8, 1024 (1928).

¹¹¹ Balderrey, F. C. and Barkus, O., *Am. Rev. Tuberculosis*, 9, 107 (1924).

¹¹² Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, 86, 1 (1928); *J. Nutrition*, 3, 465 (1931); *Chem. Abs.*, 25, 2461 (1931).

cent during the irradiation, with recovery usually within five hours after each exposure. Leucocytosis resulted from moderate irradiation but markedly low levels in the white blood cell counts followed strong excessive exposures.¹¹³ Excessive irradiation also appeared to destroy red blood cells. In experimental anemias of animals, there seems to be a more rapid restoration of the red cells after ultraviolet irradiation, although too much or too frequent irradiation seems to be definitely harmful.¹¹⁴ Although the number of red blood cells and the number of reticulocytes increased as a result of irradiation by the flaming carbon arc, the corpuscular volume and the corpuscular hemoglobin did not. In fact, the hemoglobin was practically unaltered. On the other hand, in hemolytic anemia produced by phenylhydrazine, a regeneration of hemoglobin was observed.¹¹⁵ In nutritional anemias, as the milk anemias, results with the carbon arc were negative, but with the quartz mercury arc, Foster¹¹⁶ obtained some evidence of a beneficial effect. The number, size, and saturation of the red cells were increased.

Cramer and Drew found light to act as a stimulus to the formation of blood platelets. This has been confirmed by others, including Hardy,¹¹⁷ Steiner and Gunn,¹¹⁸ and, in new-born infants, Sanford.¹¹⁹

Friedlander and Wiedemer¹²⁰ note that in healthy persons the reticulocytes (young red cells) increase in the spring months as contrasted with the count during the winter. They attribute this to an increase in ultraviolet rays from the sun. Seyderhelm,¹²¹ has claimed that dog blood upon ultraviolet irradiation develops the property of causing a sudden outpouring of erythrocytes into the blood of dogs made artificially anemic by saponins. The active substance is associated with the stroma of the irradiated red cells. Normal blood contains small quantities of this active substance. Similar results were obtained in human subjects upon the intramuscular injection of irradiated human cells, the reticulocytosis reaching its maximum one to five hours after the injection. The results in pernicious anemia are not as permanent as those obtained with liver. According to Zaepffel,¹²² rapid blood regeneration may be produced in anemic rabbits or patients by the oral administration of solutions obtained by digesting red blood cells with pancreatin followed by exposure to strong ultraviolet light. The final product contained histidine, tryptophane and hematin.

Goldberg¹²³ found parenteral administration of solutions obtained by irradiating copper or iron plates in water with ultraviolet rays to accelerate the regenerative processes in rabbits made anemic by bleeding. The local anaphylactic reaction is depressed by the use of ultraviolet-treated metals. These materials also produce capillary dilatation in frogs when injected subcutaneously.¹²⁴

¹¹³ See also Clark, J., *Physiol. Rev.*, 2, 285 (1922); Koopman, J., *Deut. med. Wochschr.*, 50, 277 (1924).

¹¹⁴ Hobert, H., *Klin. Wochschr.*, 2, 1213 (1923); *Chem. Abs.*, 17, 3893 (1923).

¹¹⁵ Mayerson, H. S., and Laurens, H., *J. Nutrition*, 4, 351 (1931); see also Kasatkin, E. V., and Bogdanova, G. P., *Arch. sci. biol. (U.S.S.R.)*, 40, No. 1, 49 (1936); *Chem. Abs.*, 37, 6679 (1937).

¹¹⁶ Foster, P. C., *J. Nutrition*, 4, 517 (1931); *Chem. Abs.*, 26, 3008 (1932).

¹¹⁷ Hardy, M., *loc. cit.*

¹¹⁸ Steiner, F. E., and Gunn, F. D., *Arch. Path.*, 11, 241 (1931); *Chem. Abs.*, 25, 4563 (1931).

¹¹⁹ Sanford, H. N., *Am. J. Diseases Children*, 83, 50 (1927).

¹²⁰ Friedlander, R., and Wiedemer, C., *Arch. Int. Med.*, 44, 209 (1929).

¹²¹ Seyderhelm, R., *Klin. Wochschr.*, 11, 628 (1932); *Chem. Abs.*, 26, 4856 (1932).

¹²² Zaepffel, H., *Bull. acad. med.*, 113, 679 (1935); *Chem. Abs.*, 30, 7657 (1936).

¹²³ Goldberg, I. M., *Acta. Med. Scand.*, 85, 136, 147 (1935); Goldberg, I. M., and Boudyline, V. G., *Ibid.*, 147.

¹²⁴ Boudyline, V. G., *Acta. Med. Scand.*, 86, 88, 95 (1935); see also Griegel, C. R., *Klin. Wochschr.*, 45, 705 (1936).

Toyoda¹²⁶ finds that irradiation of rabbits produces thrombocytogenesis, and a histamine-like substance is believed to be produced in the blood, which acts on the spleen. When the irradiation is repeated more than about five times, thrombopenia results. Such thrombopenic rabbits will again show thrombocytogenesis if a fresh spleen is grafted. When the spleen of a thrombopenic rabbit is grafted to normal splenectomized rabbits, irradiation produces no change in thrombocytes.

According to Tokumitsu and Toyota¹²⁶ the number of platelets increases in the normal rabbit within an hour after irradiation with rays between 3130 and 3900 Å, and returns to normal after two to four hours. It does not increase in splenectomized rabbits. In parathyroidectomized rabbits, the increase is more marked than in normal ones. These authors suggest that there exists a specific splenic hormone, which controls thrombocytosis and that its liberation from the spleen is controlled by a histamine-like substance produced in the skin during irradiation. In splenectomized animals the thrombocytosis on irradiation could be observed if normal spleen had been grafted into the animals.

Koh¹²⁷ noted that when a rabbit has been irradiated by these wave-lengths for an hour, erythrocytes and hemoglobin are increased in the ear vein within five hours, but they are decreased in the liver and spleen. No reticulocyte increase was noted in any veins. The effect is not due to a regeneration of the corpuscles but rather to an alteration in their distribution. This polerythemia of the ear veins can be produced in animals from which the thyroid, but not in those from which the spleen, has been removed. It is suggested that the thyroid has a hormone which antagonizes the splenic hormone and that the former is concerned with the redistribution of erythrocytes after the irradiation. Carnielli reports that irradiation of rats and guinea pigs produces a considerable increase of the oxidase in the leucocytes.¹²⁸

Recently there have been many determinations of the ultraviolet absorption of blood, its plasma and serum, and attempts have been made to correlate variations in the absorption spectra with diseased conditions. These are not discussed, since they have not as yet led to any very useful results and because our subject matter is limited to effects dependent upon the occurrence of photochemical processes.

Macht and Blackman¹²⁹ noted that animals poisoned with carbon monoxide and exposed to ultraviolet rays recovered more quickly than controls poisoned to the same degree and kept in darkness. This was attributed to the photodissociation of the carbon monoxide-hemoglobin. Estler,¹³⁰ however, was unable to verify these observations and concluded that the *in vitro* dissociation of the complex with hemoglobin had no counterpart *in vivo*. Gorkin finds the dissociation can be affected by daylight, but not by ultraviolet light.¹³¹

Harris¹³² finds that irradiation of blood causes it to give up oxygen at high oxygen tensions and to take it up at low tensions. Both effects are irreversible in darkness. At about 15 mm. tension of oxygen there is gaseous equilibrium. The taking up of the oxygen by blood in ultraviolet light he believed to be a property of the plasma. In the presence of traces of certain sensitizing substances, iron chloride, dyes, and especially hematoporphyrin and chlorophyll, the velocity of the photooxidation of plasma may be increased up to a hundred fold. The accelerating effect of hematoporphyrin is unaffected by the addition of sodium cyanide. It was noted in Chapter 34 that certain proteins and the aromatic amino-acids undergo a similar photooxidation. Krebs¹³³ finds that light affects the hemin

¹²⁶ Toyoda, G., *J. Chosen Med. Assoc.*, **22**, 673 (1932); **26**, 856, 1017 (1936); *Chem. Abs.*, **31**, 1869 (1937).

¹²⁶ Tokumitsu, Y., and Toyota, G., *Trans. Japan. Path. Soc.*, **21**, 191 (1931); *Chem. Abs.*, **26**, 6003 (1932).

¹²⁷ Koh, M., *J. Chosen Med. Assoc.*, **22**, 775 (1932); *Chem. Abs.*, **27**, 2197 (1933).

¹²⁸ Carnielli, P., *Biochem. terap. sper.*, **25**, 1 (1938); *Chem. Abs.*, **32**, 4183 (1938).

¹²⁹ Macht, D. I., and Blackman, S. S., Jr., *J. Pharmacol.*, **23**, Proc. 142 (1924); *Chem. Abs.*, **18**, 3228 (1924).

¹³⁰ Estler, W., *Arch. Hyg. Bakt.*, **115**, 152 (1936); *Chem. Abs.*, **30**, 3096 (1936).

¹³¹ Gorkin, Z. D., *J. Physiol. (U.S.S.R.)*, **22**, 329 (1937); *Chem. Abs.*, **32**, 9103 (1938).

¹³² Harris, D. T., *Biochem. J.*, **20**, 280, 271 (1926).

¹³³ Krebs, H. A., *Biochem. Z.*, **193**, 347 (1928).

catalysis of the oxidation of cysteine to cystine by molecular oxygen in the same way that it affects the respiration of living systems.

The oxygen consumption of red blood cells (and also of yeast cells) in Tyrode's solution at pH 7.2 may be increased by 50 per cent during irradiation by ultraviolet light, according to Surányi and Vermes.¹⁸⁴ Cyanide irreversibly inhibits both the normal and the increased respiration.

Hemolysis. Suspensions of red blood cells are slowly hemolyzed by visible light.¹⁸⁵ Meyerstein¹⁸⁶ found human cells which in physiological salt solution were hemolyzed in 13 to 14 days in darkness, hemolyzed in 5 to 6 days in light. Radiations of wave-lengths less than 2700Å are more effective, according to Koeppe.¹⁸⁷ Hausmann and Sonne¹⁸⁸ found it possible to sensitize the cells to the longer wave-lengths of the ultraviolet by means of hematoporphyrin. The effect is then most marked at 3130Å. *In vivo* this effect could not be demonstrated. Löhner¹⁸⁹ found arsenious acid to sensitize red blood cells to either visible or ultraviolet light. Fabre and Simonnet¹⁴⁰ state that cholesterol-free lecithin, if irradiated in the presence of hematoporphyrin by ultraviolet light, undergoes a change by which it acquires a greater hemolytic power than it can attain on unsensitized irradiation.

During the irradiation of normal persons a gain in fecal urobilin was observed by Teplov and Mesheristkaya.¹⁴¹ This was attributed to increased hemolysis. At the same time the production of red cells was stimulated, so that the total number of red cells and the hemoglobin content of the blood usually remained constant. In anemic subjects, the apparent regeneration of the blood is explained by an overcompensation which causes the rate of the production of blood to exceed the rate of hemolysis. At the conclusion of the treatment, the rate of hemolysis sinks rapidly to normal, and the overproduction of red cells also subsides.

Farkas and Tangl¹⁴² had noted, on the contrary, that in dogs, unless splenectomized, ultraviolet irradiation inhibits the passing out of their blood pigment.

Ward¹⁴³ has claimed that the influenza bacillus when grown on blood-agar plates is unable to produce hemolysis if incubated in darkness. If it is then exposed to sunlight or artificial light, it shows a definite hemolysis after a time which depends upon the intensity of the light.

The permeability of erythrocytes to water-soluble substances, such as glycerol, glucose, etc., is said to be increased by light.¹⁴⁴ The spectral distribution of the efficiency of radiation in decreasing the stability of the red cells corresponds very closely to that of the absorption of radiations by oxyhemoglobin.¹⁴⁵ This suggests that the effect is exerted upon the hemoglobin rather than upon the colorless cell membrane.

Although hematin and hemochromogen are not altered by sulfur dioxide in

¹⁸⁴ Surányi, G., and Vermes, M., *Magyar Orvosi Arch.*, 30, 585 (1929); *Chem. Abs.*, 25, 2162 (1931).

¹⁸⁵ Hausmann, W., and Loewy, A., *Biochem. Z.*, 173, 1 (1926); Earle, W. R., *J. Exptl. Med.*, 48, 457, 667, 583 (1928); Lepeschkin, W. W., *Science*, 73, 568 (1931).

¹⁸⁶ Meyerstein, *Klin. Wochschr.*, 7, 2244 (1928); *Chem. Abs.*, 23, 1438 (1929).

¹⁸⁷ Koeppe, H., *Arch. Kinderheilk.*, 79, 109, 198 (1926).

¹⁸⁸ Hausmann, W., and Sonne, C., *Strahlentherapie*, 25, 174 (1927).

¹⁸⁹ Löhner, L., *Biochem. Z.*, 186, 194 (1927).

¹⁴⁰ Fabre, R., and Simonnet, H., *Compt. rend.*, 184, 707 (1927).

¹⁴¹ Teplov, I., and Mesheristkaya, R., *Deut. Arch. Klin. Med.*, 174, 399 (1933); *Chem. Abs.*, 27, 5347 (1933).

¹⁴² Farkas, G., and Tangl, H., *Biochem. Z.*, 200, 184 (1928); *Chem. Abs.*, 23, 168 (1929).

¹⁴³ Ward, H. K., *J. Bacteriol.*, 15, 51 (1928).

¹⁴⁴ Lepeschkin, W. W., *Protoplasma*, 18, 243 (1933); *Chem. Abs.*, 27, 3228 (1933).

¹⁴⁵ Lepeschkin, W. W., and Davis, G. E., *Protoplasma*, 20, 188 (1933); *Chem. Abs.*, 28, 1722 (1934).

darkness, when illuminated with this compound they lose iron and are converted into hematoporphyrin-like substances. These differ from Nencki's hematoporphyrin in their sulfur content and in their solubility, according to Zeynek and Kittel.¹⁴⁶ Under similar conditions, blood pigments also lose their iron and are converted into porphyrin-proteoses, containing varying amounts of more or less firmly bound proteins. Light sensitization of white mice by these products differs little from sensitization by Nencki's hematoporphyrin.

Vital staining in the red cells of frogs is said to be materially retarded by light rays of the shorter wave-length half of the visible spectrum.¹⁴⁷

Falk and Reed¹⁴⁸ found that in blood directly irradiated *in vivo*, there is a small but definite decrease in the negative electrophoretic potential of the red cells.

Blood Sugar and Carbohydrate Metabolism. Frenkel-Tissot¹⁴⁹ believed, as a result of studies at high altitudes, that people with high blood sugar tend to have this decreased by irradiation by the sun or the mercury arc or by hyperthermia, although those with normal or low blood sugar values show a tendency for the sugar to be increased by the same treatments. Many subsequent observers have noted a depression of the blood sugar on irradiation.¹⁵⁰ Petersen and v. Oettingen¹⁵¹ found that in dogs a short exposure was as effective as a longer one in causing a reduction in the amounts of sugar and chlorides in the lymph, an increase in the number of white cells in the blood, and in the volume and protein content of the lymph.

When blood is directly irradiated in quartz tubes *in vivo* by the method of Reed, in anesthetized dogs, the blood sugar is not affected.¹⁵² Treatment of guinea pigs, cats and dogs with serum which had been previously irradiated in most cases reduced the elimination of sugar by the liver.¹⁵³

Keeser¹⁵⁴ observed that rabbits placed in blue light and injected intravenously with glucose show a less pronounced and shorter hyperglucemia than those injected in daylight. Irradiation also causes an increased content of sugar in the skin. There is also a marked decrease of from 31 to 15 mg. per cent in the reduced glutathione content of the skin and a smaller decrease in that of the blood. Keeser¹⁵⁵ believes blue light to have a sympathicotonic and red light a vagotonic action.

Ogawa¹⁵⁶ found the reduced glutathione in both arterial and venous blood of irradiated rabbits to be decreased immediately after irradiation. After thirty to sixty minutes, however, it increased markedly. The same was true of the content of the oxidized form in arterial blood, but in the venous blood it increased immediately after the irradiation.

¹⁴⁶ Zeynek, R., and Kittel, S., *Z. physiol. Chem.*, **224**, 233 (1934); *Chem. Abs.*, **28**, 4079 (1934).

¹⁴⁷ Kedrovskii, B., *Protoplasma*, **22**, 607 (1935); *Chem. Abs.*, **29**, 3362 (1935).

¹⁴⁸ Falk, I. S., and Reed, C. I., *Am. J. Physiol.*, **75**, 616 (1926).

¹⁴⁹ Frenkel-Tissot, H. C., *Deut. Arch. Klin. Med.*, **133**, 286 (1920); *Chem. Abs.*, **15**, 118 (1921).

¹⁵⁰ Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928); Bloch, C. E., and Faber F., *Am. J. Dis. Children*, **30**, 504 (1925); Rothmann, H., *Klin. Wochschr.*, **2**, 881 (1923); Pincussen, L., and Yakota, S., *Biochem. Z.*, **241**, 398 (1931); Pincussen, L., *Biochem. Z.*, **272**, 354 (1934); *Klin. Wochschr.*, **10**, 791 (1933); **11**, 1231 (1932); *Chem. Abs.*, **26**, 5612 (1932); *Strahlentherapie*, **51**, 537 (1934).

¹⁵¹ Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmacol.*, **123**, 160 (1927); *Chem. Abs.*, **22**, 276 (1928).

¹⁵² Reed, C. I., Payte, J. I., and Lackey, R. W., *Proc. Soc. Exptl. Biol. Med.*, **24**, 11 (1926).

¹⁵³ Holtz, P., *Arch. Ges. Physiol. (Pflüger's)*, **226**, 578 (1931); *Chem. Abs.*, **25**, 2194 (1931).

¹⁵⁴ Keeser, E., *Arch. Exptl. Path. Pharmacol.*, **166**, 624 (1932).

¹⁵⁵ See also von Deschwander, J., who attributes the results to increased insulin formation; [*Strahlentherapie*, **39**, 278 (1931); *Chem. Abs.*, **25**, 1886 (1931); *Strahlentherapie*, **46**, 713 (1933); *Chem. Abs.*, **21**, 3489 (1933)].

¹⁵⁶ Ogawa, M., *J. Agr. Chem. Soc. Japan*, **13**, 81 (1937); *Chem. Abs.*, **31**, 3077 (1937).

Jona¹⁵⁷ gave progressively increasing daily irradiations to four normal persons and two diabetics for a month. In the normal persons there was a diminution in glucemia but no notable effect on the glucose tolerance or glycosuria. In the diabetics it was found that although both the glucemia and glycosuria were diminished, the general condition of the patients was adversely affected and the acetonuria increased.

Gorini¹⁵⁸ finds that small doses of ultraviolet rays enhance the glucose metabolism and large doses depress it. In infants and children, the blood sugar is increased by ten minutes and reduced by twenty minutes of irradiation or by the use of greater intensities, according to Ferri.¹⁵⁹ In alimentary hyperglucemia, the reaction is hastened by short and retarded by long exposures, but adrenalin hyperglucemia is always enhanced by irradiation. Ceruti¹⁶⁰ determined the glucemic titer before and after the irradiation of albino rats. In a group exposed to the direct rays of the mercury-vapor lamp for 15, 30 and 60 minutes, there was an average diminution of 10, 25 and 31 per cent respectively. In a group exposed with a Wood glass filter the values were 8, 13, and 18 per cent, and in a third group in direct sunlight, 6, 9 and 12 per cent.

Kallós and Kallós-Deffner¹⁶¹ found that ultraviolet light lowered the fasting blood sugar and increased the sugar tolerance of rabbits which had been previously kept in darkness for a week.¹⁶² On the other hand, Müller¹⁶³ found no difference in the blood sugar level of rabbits kept in darkness for two or three weeks from that of those kept in the light. Nor could a difference in the glucose tolerance be detected.

Ventral irradiation is said to be more effective than dorsal in producing a constant and progressive decrease in the blood sugar of rabbits by Benvenuto,¹⁶⁴ who did not succeed, however, in demonstrating an effect upon the glucose tolerance. Besides noting a decrease in the blood sugar which reaches its maximum at the height of the erythema, Marchionini and Hövelborn¹⁶⁵ found the blood diastase to be increased by ultraviolet irradiation.

Burge and Wickwire¹⁶⁶ find that the normal rate of utilization of glucose and galactose by *Paramecium caudatum* is depressed by ultraviolet irradiation. This effect is abolished by the addition of insulin to the medium and was thought to be due to the destruction of insulin in the living cells by the irradiation.

Pincussen and Jacoby¹⁶⁷ find the lactic acid content of the whole blood of rabbits to decrease by 20 to 30 per cent shortly after an irradiation. The content in the serum, however, increases. The authors suggest that during irradiation the permeability of the corpuscles may increase so as to permit the passage of a considerable part of their lactic acid into the serum. The glycogen of heart and muscle, if changed at all, decreases slightly, although the total carbohydrate increases considerably. It appears therefore, that irradiation causes a sparing of

¹⁵⁷ Jona, A., *Minerva Med.*, **II**, 757 (1933); *Chem. Abs.*, **28**, 1401 (1934).

¹⁵⁸ Gorini, P., *Pediatria Rivista*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).

¹⁵⁹ Ferri, U., *Riv. clin. pediatr.*, **25**, 217 (1927); *Chem. Abs.*, **22**, 619 (1928).

¹⁶⁰ Ceruti, G., *Boll. soc. ital. biol. sper.*, **3**, 30 (1928); *Chem. Abs.*, **22**, 2383 (1928).

¹⁶¹ Kallós, P., and Kallós-Deffner, L., *Strahlentherapie*, **50**, 191 (1934); *Chem. Abs.*, **28**, 4772 (1934). See also Root, R. W., *Arch. Phys. Therapy, X-Rays, Radium*, **12**, 153 (1931); *Chem. Abs.*, **26**, 1648 (1932).

¹⁶² See also Rothman, S., *Strahlentherapie*, **51**, 364 (1934); Pincussen, L., *Ibid.*, **53**, 7 (1934).

¹⁶³ Müller, R. W. J., *Biochem. Z.*, **276**, 416 (1935).

¹⁶⁴ Benvenuto, E., *Pediatria Riv.*, **43**, 675 (1915); *Chem. Abs.*, **30**, 4182 (1936).

¹⁶⁵ Marchionini, A., and Hövelborn, C., *Klin. Wochschr.*, **14**, 1387 (1935); *Chem. Abs.*, **30**, 2997 (1936).

¹⁶⁶ Burge, W. E., and Wickwire, G. C., *J. Biol. Chem.*, **72**, 827 (1927).

¹⁶⁷ Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928).

sugar but it was uncertain whether this was due to a decreased breakdown of the sugar or to an increased formation of sugar from lactic acid. Later, however, Pincussen and Kawakami¹⁶⁸ stated that in the liver and muscles of irradiated animals there is an increase in glycogen at the expense of lactic acid. The glycogen:lactic acid ratio is raised 55 and 45 per cent in the liver and muscles, respectively, but in the heart the change does not exceed the experimental error. They believe the radiations to act in a manner similar to that of insulin.

By irradiating muscle extract before incubation, Stiven¹⁶⁹ has found it possible to increase the rate of lactic acid formation from glycogen. In one case the rate of lactic acid formation in the irradiated sample was three times that in the control. Irradiation leads also to alterations of the accumulation of the phosphoric ester. Brief irradiations resulted in an increase of the ester accumulation, but longer ones produced a decrease. The higher rates of lactic acid formation coincide with a decrease in the ester accumulation. In only one of thirteen experiments was the lactic acid formation decreased after a long irradiation, and in this case the accumulation of ester was almost completely inhibited.

Blood pH. During the first hour after irradiation, there is a transient blood acidosis in human subjects, according to Kroetz.¹⁷⁰ This amounts to a drop of about 0.3 to 0.7 in pH and is ascribed by Kroetz to introduction into the blood of the altered proteins or their disintegration products formed as a result of the irradiation. This phase is followed by a more permanent alkalosis reached about 24 hours after the exposure. In it, the blood pH is raised about 0.05 to 0.07 unit above normal. This is ascribed to shifts of bases from the tissues to the blood. During the stage of acidosis, the blood is hydrated, but in the later stages the serum becomes more concentrated. In the early acidosis, the respiratory center is stimulated and there may be some hyperventilation. The alteration of the ionic equilibrium in the serum of the irradiated individual is summarized as an increase in the ratio $K^+ \times (H_2PO_4' + HPO_4'') / Ca^{++}$. Refractometric measurements revealed an alteration in the nature of the serum proteins. The early increase in blood acidity was also obtained as a result of the *in vitro* irradiation of blood. Hoeber¹⁷¹ found ultraviolet light to render horse serum more acid. On the other hand, Moran and Reed¹⁷² found irradiation of dog blood *in vivo* to fail to produce any constant effect on the carbon dioxide combining power.

According to Balderrey and Barkus¹⁷³ exposure of the human body to sunlight increases the alkalinity of the blood. The amount of pigmentation present has a direct influence on the change of the blood reaction, the greater the amount of pigmentation the more marked being the change in the blood pH. In their experiments, the effects were probably to be attributed predominantly to radiations of the visible spectrum. Variations in the intensity of the light materially influenced its effects on the blood reaction.

In earlier studies, Ederer¹⁷⁴ determined the influence of the light of a quartz lamp upon the alveolar carbon dioxide tension of man. The results varied with the

¹⁶⁸ Pincussen, L., and Kawakami, T., *Biochem. Z.*, **208**, 185 (1929); Pincussen, L., *Arch. Phys. Therapy, X-Ray, Radium*, **18**, 750 (1937); *Chem. Abs.*, **32**, 4615 (1938).

¹⁶⁹ Stiven, D., *Biochem. J.*, **24**, 172 (1930).

¹⁷⁰ Kroetz, C., *Biochem. Z.*, **151**, 146, 449 (1924).

¹⁷¹ Hoeber, R., *La Med. Germano-Ispano Amer.*, **1**, 113 (1923); *Physiol. Abs.*, **10**, 61; *Chem. Abs.*, **19**, 3115 (1925); see also Frontali, G., *Rev. Clin. Pediatr.*, **25**, 661 (1927); *Chem. Abs.*, **23**, 1657 (1929). There is a slight decrease in total nitrogen and albumin nitrogen and an increase in the globulin nitrogen, according to Murayama, M., *J. Oriental Med.*, **34**, 79 (1936); *Chem. Abs.*, **31**, 5820 (1937).

¹⁷² Moran, W. H., and Reed, C. J., *Proc. Soc. Exptl. Biol. Med.*, **24**, 179 (1926).

¹⁷³ Balderrey, F. C., and Barkus, O., *Am. Rev. Tuberculosis*, **9**, 107 (1924).

¹⁷⁴ Ederer, S., *Biochem. Z.*, **132**, 103 (1922); *Chem. Abs.*, **17**, 303 (1923).

dosage administered. Weak stimulation had no effect. Radiations of medium intensity increased the carbon dioxide tension but strong irradiation lowered it. The effects appeared to be independent of the skin erythema. The hypercapnic effect was considered to be hemogenous and not of central origin. This interpretation was based upon a belief, then undemonstrated, in a probable increase in the alkalinity of the blood, a decrease in the acid products of metabolism and a change in the colloidal state of the blood proteins.

Glass¹⁷⁵ observed for two to four hours after intense ultraviolet treatment, a change in the chlorine distribution in the blood, which was regarded as an indication of a shift in the acid-base equilibrium in the blood toward an acidotic condition. This sometimes persisted for 24 hours.

The analysis of urine samples during an hour after a single irradiation failed to indicate to Essinger and György¹⁷⁶ any shift in the acid-base equilibrium. The serum calcium was slightly decreased.

Iancou and Iana¹⁷⁷ determined the pH of the blood serum of eleven nursing mothers at the beginning, middle and end of a period of irradiation of the mammary glands. In seven, it rose appreciably, in one it remained constant, in two it at first dropped slightly and then returned to its initial value and in one suffering from an infection it dropped very slightly. In six cases the calcium content rose appreciably and in the other five it dropped slightly. The action on the nurslings was even less pronounced, unstable and inconstant. Lenzi¹⁷⁸ believes irradiation to cause no change in the blood pH.

The effects of general body irradiation upon other features of the blood composition have been frequently studied. In normal subjects, no very pronounced changes in phosphorus in its various forms, chlorine, magnesium, calcium, sodium or potassium have been found. Slight positive or negative variations may be produced at various periods during or after irradiation, but rarely have marked changes been observed.¹⁷⁹

Frontali¹⁸⁰ noted an increase in the inorganic phosphorus of serum which had been irradiated fifteen to sixty minutes by a mercury arc. Sacchi¹⁸¹ observed a decrease in the phosphatase content of the bones of rats kept in darkness, which could be restored to normal by exposing them to direct sunlight for a week.

In the *in vivo* irradiation of blood streaming through a quartz tube interposed in the circulation, Reed and Tweedy¹⁸² found no immediate changes in the blood

¹⁷⁵ Glass, J., *Biochem. Z.*, 231, 45 (1931); *Chem. Abs.*, 25, 2160 (1931).

¹⁷⁶ Essinger, R., and György, P., *Biochem. Z.*, 149, 344 (1924).

¹⁷⁷ Iancou, A., and Iana, I., *Bull. soc. péd.*, 30, 76 (1932); *Chem. Abs.*, 27, 3729 (1933).

¹⁷⁸ Lenzi, F., *Biochim. terap. sper.*, 23, 118 (1936); *Chem. Abs.*, 30, 6018, 6772 (1936).

¹⁷⁹ Lodenkämper, H., *Balneologie*, 1, 438 (1934); *Chem. Abs.*, 31, 3948 (1937); Kroetz, C., *Biochem. Z.*, 151, 449 (1924); Malczynski, S., *Compt. rend. soc. biol.*, 113, 1297 (1923); *Chem. Abs.*, 27, 5345 (1933); Pincussen, L., and Makrinos, I., *Biochem. Z.*, 161, 61, 67 (1925); Mayerson, H. S., Gunther, L., and Laurens, H., *Proc. Soc. Exptl. Biol. Med.*, 22, 469 (1925); Bomskov, C., and von Rose, M., *Klin. Wochschr.*, 10, 1956 (1931); *Chem. Abs.*, 26, 2495 (1932); Malczynski, S., Borsiewicz, A., and Toczyński, T., *Compt. rend. soc. biol.*, 108, 165 (1931); *Chem. Abs.*, 26, 2754 (1932); von Rose, M., *Z. Kinderheilk.*, 54, 236 (1933); *Chem. Abs.*, 27, 2985 (1933); Egidi, E., and Rowinski, P., *Boll. soc. ital. biol. sper.*, 9, 118 (1934); *Chem. Abs.*, 28, 3746 (1934); Stiemens, H., and Heringa, G., *Nederland. Tijdschr. Geneeskund.*, 77, II, 1635 (1933); *Chem. Abs.*, 28, 2732 (1934); Brown, W. H., and Howard, M., *J. Exptl. Med.*, 49, 103 (1929); Fairhall, L. T., *Am. J. Physiol.*, 84, 378 (1928); Maynard, L. A., Goldberg, S. A., and Miller, R. C., *Proc. Soc. Exptl. Biol. Med.*, 22, 494 (1925); Orr, J. B., Magee, H. E., and Henderson, J. M., *J. Physiol.*, 70, Proc. 25 (1924); Howe, M. G., and Medlar, E. M., *Am. Rev. Tuberculosis*, 10, 408 (1924); Moritz, A. R., *J. Biol. Chem.*, 64, 81 (1925); Cheymol, J., and Quinquaud, A., *J. pharm. chim.*, 16, 233 (1932); *Chem. Abs.*, 27, 1901 (1933); Pincussen, L., *Biochem. Z.*, 182, 359 (1927).

¹⁸⁰ Frontali, G., *Riv. Clin. Pediatr.*, 25, 661 (1927); *Chem. Abs.*, 23, 1657 (1929); also De Toni, G., and Stancati, A., *Boll. soc. ital. biol. sper.*, 4, 163 (1929); *Chem. Abs.*, 23, 3721 (1929); Careddu, G., *Biochim. terap. sper.*, 18, 109 (1931); *Chem. Abs.*, 25, 4015 (1931).

¹⁸¹ Sacchi, U., *Boll. soc. ital. biol. sper.*, 9, 94 (1935); *Chem. Abs.*, 29, 4781 (1935).

¹⁸² Reed, C. I., and Tweedy, W. R., *Am. J. Physiol.*, 76, 54 (1926).

calcium. No effects upon the diffusibility of the serum calcium could be observed to follow either the irradiation of an animal or of its serum directly, by Moritz.¹⁸³ The addition of calcium chloride to rabbit serum, previously irradiated either *in vivo* or *in vitro*, is said to depress its electrical conductivity; the effect is not observed in the absence of the preceding irradiation.¹⁸⁴

In marked contrast to the observations upon normal subjects are the results obtained in rachitic animals discussed in Chapter 38. The irradiation of normal rabbits was found by Grant and Gates¹⁸⁵ to cause an hypertrophy of the parathyroids. Nonidez and Goodale¹⁸⁶ found that when young chicks were kept on a ration poor in vitamin C and deprived of direct sunlight, an enlargement of the parathyroid gland resulted. It was due to an increase in the size and number of epithelial cells. This was followed by a phase of regression and in some cases by local degenerative changes. Subsequent exposure to sunlight led to a decrease of the gland volume with a considerable crowding of the epithelial cells and sometimes to pressure atrophy.

The irradiation of parathyroidectomized dogs did not significantly increase their blood calcium level, according to Swingle and Rhinhold.¹⁸⁷ Jung¹⁸⁸ however, found daily doses of ultraviolet light fifty times those commonly applied to unhabituated human subjects, to benefit parathyroidectomized white rats. He believed the parathyroid to have some function related to the photochemistry of the skin. Drucker and Faber¹⁸⁹ found that irradiation during tetany brought the calcium to a normal level without changing the blood pH or affecting the antagonistic relation between phosphorus and calcium. The increase in total serum calcium does not occur immediately following the irradiation of children with tetany as is the case with inorganic phosphorus. Indeed, it comes subsequent to the effects on the tetany. Calcium in the ultrafiltrate is generally below 50 per cent of the total calcium before irradiation. It increases in successive determinations and comes to exceed 60 per cent of the total calcium. Later a gradual increase in total calcium ensues.¹⁹⁰

Although Malczynski¹⁹¹ found a considerable increase in the blood cholesterol of irradiated human subjects, Ornstein found no significant changes.¹⁹² Pincussen and Zuckerstein¹⁹³ found the serum cholesterol unchanged in irradiated animals, although the total ether extract of the serum was definitely increased. In rabbits, Kultjugin¹⁹⁴ found irradiation to increase the cholesterol not over 30 per cent, although the blood fat was greatly increased after the second exposure.

Hubert¹⁹⁵ believes that patients with carcinoma usually show a decrease in the serum cholesterol after irradiation. There are, however, so many exceptions that it is unlikely that this response to irradiation can have diagnostic significance.

¹⁸³ Moritz, A. R., *J. Biol. Chem.*, **64**, 81 (1925).

¹⁸⁴ Dell Aquila, A., and Jais, F., *Arch. farmacol. sper.*, **60**, 578 (1935); *Chém. Abs.*, **30**, 4520 (1936).

¹⁸⁵ Grant, J. H. B., and Gates, F. L., *Proc. Soc. Exptl. Biol. Med.*, **21**, 230 (1924); *J. Exptl. Med.*, **45**, 115 (1927).

¹⁸⁶ Nonidez, J. F., and Goodale, H. D., *Am. J. Anatomy*, **38**, 319 (1927); *Chem. Abs.*, **21**, 2016 (1927).

¹⁸⁷ Swingle, W. W., and Rhinhold, J. S., *Am. J. Physiol.*, **75**, 59 (1925).

¹⁸⁸ Jung, F. T., *Endocrinology*, **12**, 81 (1928); *Chem. Abs.*, **22**, 2575 (1928); see also Vines, H., *Endocrinology*, **11**, 125 (1927); *Chem. Abs.*, **21**, 3960 (1927).

¹⁸⁹ Drucker, P., and Faber, F., *J. Biol. Chem.*, **68**, 57 (1926).

¹⁹⁰ Careddu, G., *Atti soc. med. Padova*, **15**, 126 (1937); *Chem. Abs.*, **32**, 6273 (1938).

¹⁹¹ Malczynski, S., *Compt. rend. soc. biol.*, **99**, 922 (1928); *Chem. Abs.*, **23**, 401 (1929).

¹⁹² Ornstein, T., *Compt. rend. soc. biol.*, **103**, 190 (1930); *Chem. Abs.*, **25**, 117 (1931).

¹⁹³ Pincussen, L., and Zuckerstein, E., *Biochem. Z.*, **207**, 426 (1929).

¹⁹⁴ Kultjugin, A., *Biochem. Z.*, **186**, 36 (1927).

¹⁹⁵ Hubert, R., *Arch. Gynäkol.*, **146**, 51 (1931); *Chem. Abs.*, **25**, 5926 (1931); *Arch. Gynäkol.*, **149**, 433 (1932); **151**, 681 (1932); *Chem. Abs.*, **27**, 2462 (1933).

The total blood sulfur is said to be lowered after ten minutes of irradiation.¹⁹⁶ Free sulfur and oxidized sulfur diminished in a parallel manner, but the former much more rapidly than the latter, so that the ratio of oxidized sulfur to total sulfur was, in general, increased.¹⁹⁷

In vitro irradiation of human blood serum lowers its surface tension, although the results of *in vivo* irradiation are uncertain.¹⁹⁸ The index of refraction of normal horse serum at 20°C. increased progressively from 1.3466 to 1.3531 during thirty minutes of irradiation. Beef plasma showed a similar behavior and there were similar increases in antitetanic, antistreptococcic and antidiphtheric sera.¹⁹⁹ The change is attributed to an alteration of the state of the proteins.

The gelatinization of serum is said to be accelerated by ultraviolet rays.²⁰⁰

An acceleration of the rate of red cell sedimentation is produced over only a limited range of dosages, beyond which the rate tends to be retarded.²⁰¹

The blood and skin of rabbits which have been irradiated over a period of three to six weeks is found by Engel²⁰² to contain a substance which induces cornification in castrated female mice. Its formation is not promoted by the simultaneous injection of cholesterol. Ultraviolet irradiation of castrated female rats and mice does not produce a positive Allen-Doisy test.

Blood Enzymes. Pincussen²⁰³ found the activity of the blood catalase of rabbits kept in darkness slightly greater than that of animals exposed to ultraviolet light, especially if they had been given a sensitizer. In rats, the diminution is especially marked in the liver.²⁰⁴ Koldayev and Altschuller²⁰⁵ noted a transitory decrease in the serum amylase and blood catalase of irradiated rabbits. Castagna²⁰⁶ found the longer rays of sunlight to increase the blood catalase of mice over that in those kept in darkness, these having almost none. Irradiation in the wavelength range 3190 to 3900 Å did not materially change the catalase content. When both this radiation and visible light were used, the catalase content increased during the first three hours of irradiation and then declined. Daily sunbaths are said to cause a small increase in human blood catalase.²⁰⁷

The general irradiation of rabbits produces a proteinase capable of attacking skin and serum proteins, according to Abderhalden and Tetzner.²⁰⁸ Schamberg and Brown²⁰⁹ find that exposure of rabbits to ultraviolet light decreases the concentration of lipase and increases that of proteinase in the blood. In the skin, both are decreased. Vedder²¹⁰ observed that when leucocytes are irradiated with visible light, the granules which contain oxidase disappear only if the temperature is raised above 62°. Ultraviolet irradiation, however, is effective at ordinary temperatures.

¹⁹⁶ Loeper, M., Degos, R., and Lesure, A., *Compt. rend. soc. biol.*, **106**, 718 (1931); *Chem. Abs.*, **25**, 3370 (1931).

¹⁹⁷ See also Loeper, M., Decourt, J., Olivier, J., Tonnet, J., and Lesure, A., *Compt. rend. soc. biol.*, (1926-7).

¹⁹⁸ Gobel, *Biochem. Z.*, **190**, 95 (1927); Tamura, A., *Acta Schol. Med. Univ. Kyoto*, **16**, 253 (1934); *Chem. Abs.*, **28**, 4754 (1934).

¹⁹⁹ Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **98**, 978 (1928); *Chem. Abs.*, **22**, 3179 (1928).

²⁰⁰ Kopaczewski, W., *Compt. rend.*, **198**, 1947 (1934).

²⁰¹ Kostyal, L., *Biochem. Z.*, **299**, 100 (1930).

²⁰² Engel, P., *Endokrinologie*, **20**, 86 (1938); *Chem. Abs.*, **32**, 8452 (1938).

²⁰³ Pincussen, L., *Biochem. Z.*, **168**, 474 (1926).

²⁰⁴ Pincussen, L., and Tanino, F., *Biochem. Z.*, **234**, 478 (1931).

²⁰⁵ Koldayev, B., and Altschuller, M. M., *Z. physiol. Chem.*, **186**, 223 (1930).

²⁰⁶ Castagna, S., *Biochim. terap. sper.*, **13**, 48 (1926); *Chem. Abs.*, **20**, 2529 (1926); *Arch. sci. biol. ital.*, **10**, 118 (1927); *Chem. Abs.*, **22**, 97 (1928).

²⁰⁷ Deribas, D., and Kornmann, J., *Bull. soc. chim. biol.*, **18**, 418 (1936); *Chem. Abs.*, **30**, 5244 (1936).

²⁰⁸ Abderhalden, E., and Tetzner, E., *Fermentforschung*, **14**, 522 (1935); *Chem. Abs.*, **29**, 8010 (1935).

²⁰⁹ Schamberg, J. F., and Brown, H., *Arch. Int. Med.*, **35**, 537 (1925).

²¹⁰ Vedder, A., *Nederland. Tijdschr. Geneeskunde*, **68**, 2357 (1924); *Chem. Abs.*, **19**, 1143 (1924).

Effects on Immune Bodies in Blood. In general, irradiation does not affect the bactericidal properties of the blood of an irradiated subject.²¹¹ After long periods of intense ultraviolet irradiation of rabbits, Albela²¹² found no alteration of the phagocytic action of the blood serum, as determined by the concentration of opsonins. Koopman²¹³ observed that although the complement of the blood of a guinea pig was almost doubled during the first hour of irradiation of the animal, its concentration decreased markedly during a further two hours of exposure. This usually produced death and the blood was found free from complement. Gordon and Wormall²¹⁴ did not find the irradiation of guinea pigs to increase the serum complement. Osborn²¹⁵ found an occasional increase in the case of young, weaned rats, but this could not be uniformly obtained. Mesik reports a sharp drop during the irradiation, with a return to normal upon its cessation.²¹⁶

Matushita²¹⁷ found irradiation of the skin of rabbits with ultraviolet rays to increase the amount of antityphoid substance in the serum (confirmed by Mesik), an effect especially marked in the serum of immunized animals. Both the skin and the spleen were necessary for irradiation to evoke this response. Irradiation of the skin was believed to produce a histamine-like substance which causes the spleen to release a hormone that controls the production of the antityphoid substance. Bessemans and Seldeslacht²¹⁸ found that rabbits injected with an emulsion of typhoid bacilli and then treated with ultraviolet rays showed a larger production of antibodies than non-irradiated animals.

Heuer and Potthoff²¹⁹ found that an exposure of animals to ultraviolet rays had only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones. However, at the height of antibody formation, when the titer is somewhat constant, exposure of animals to ultraviolet rays causes a very great increase in the titer. This effect is not permanent and the return of the titer to the preimmunization level is much more rapid than in nonexposed animals. Wenger²²⁰ finds carbon-arc irradiation of a small area on the back of a pig sufficient to produce a slight erythema to cause a moderate increase in the bactericidal action of the blood. This effect is considerable, he believes, when the erythema is severe.

Abe finds that irradiation of black rabbits accelerates the production of the agglutinin for *B. coli*, more marked than in white rabbits.²²¹

The antityptic activity of rabbit serum is said to increase after ultraviolet irradiation.²²²

Giaume²²³ claimed that irradiated normal horse serum does not produce anaphylactic shock in sensitized guinea pigs. Five minutes of irradiation of the sensitized

²¹¹ Tataranu, F., *Compt. rend. soc. biol.*, **97**, 1736 (1927); *Chem. Abs.*, **22**, 1799 (1928).

²¹² Albela, D., *Deut. med. Wochschr.*, **48**, 1347 (1922); *Chem. Abs.*, **17**, 140 (1923).

²¹³ Koopman, J., *Deut. med. Wochschr.*, **50**, 277 (1924); *Chem. Abs.*, **18**, 2197 (1924).

²¹⁴ Gordon, J., and Wormall, A., *Biochem. J.*, **22**, 909 (1928).

²¹⁵ Osborn, T. W. B., *Biochem. J.*, **25**, 2136 (1931).

²¹⁶ Mesik, R. E., *Arch. sci. biol. (U.S.S.R.)*, **40**, 31 (1936); *Chem. Abs.*, **31**, 6726 (1937).

²¹⁷ Matushita, M., *J. Chosen Med. Assoc.*, **22**, 787 (1932); *Chem. Abs.*, **27**, 2208 (1933).

²¹⁸ Bessemans, A., and Seldeslacht, A., *Compt. rend. soc. biol.*, **99**, 628 (1928); *Chem. Abs.*, **23**, 435 (1929).

²¹⁹ Heuer, G., and Potthoff, P., *Centralbl. Parasitenk.*, **1**, 88, 299 (1922); *Chem. Abs.*, **17**, 144 (1923).

²²⁰ Wenger, W. J., *Z. Immunitat*, **93**, 501 (1938); *Chem. Abs.*, **32**, 9248 (1938).

²²¹ Abe, G., *Sei-i-kai Med. J.*, **56**, No. 11, 2169 (1937); *Chem. Abs.*, **32**, 5438 (1938).

²²² Yamanaka, G., *Sei-i-kwai*, *Med. J.*, **48**, 3, 62 (1929); *Chem. Abs.*, **23**, 4263 (1929).

²²³ Giaume, C., *Pediatria Rivista*, **35**, 1111 (1927); *Pathologica*, **20**, 236 (1928); *Chem. Abs.*, **22**, 2202 (1928).

animal lessens the shock produced by normal serum. Severe and even fatal shocks result when both the sensitizing agent and the shock-producing material have been irradiated. Brotzu²²⁴ finds daylight or light in the range 5100 to 7700Å to be more effective than blue-violet light or darkness in aiding the production of agglutinins in guinea pigs injected with the Gaertner bacillus or with the cholera vibrio. Infrared rays stimulated more agglutinin formation than daylight, and ultraviolet rays more than blue-violet light. Guinea pigs exposed to infrared rays produce more bacteriolysins than those exposed to ultraviolet light.

Exposure of guinea pigs to red, yellow or blue light has no effect on the formation of anti-sheep hemolysins.²²⁵

It has been said that serums obtained from rabbits inoculated with organisms grown on ultraviolet-irradiated agar show greater agglutinating, bacteriolytic and complement materials than those in the production of which the organisms had been grown on ordinary agar.²²⁶

There have been several recent investigations of the effect of ultraviolet light upon antigens. Intensive irradiation of horse serum for twenty to forty minutes destroys its ability to cause the characteristic anaphylactic contraction of the isolated uterus of guinea pigs sensitized to horse serum. The treated serum retains its ability to desensitize the uterus and after exposure to the treated serum, the uterine horns will no longer react with fresh, untreated serum. This sensitization, however, requires a longer period than that produced by untreated actively shocking serum.²²⁷ Different results were reported by Kitamura and Murayama²²⁸ who found 0.1 cc. of thirty minute-irradiated horse serum or egg-white to produce the usual contraction of the uterus of sensitized guinea pigs. After washing and the lapse of twenty minutes, the addition of 0.5 cc. of normal serum also produced a contraction, indicating that desensitization had not been attained. Then, after ten minutes, the addition of neither serum produced contraction.

The agglutinogens of red blood cells, which are said not to contain protein, are not affected by ultraviolet light.²²⁹

Heuer²³⁰ reported that antibodies are sensitive to ultraviolet rays when diluted. The agglutinins for cholera and paratyphoid A were believed less resistant to ultraviolet rays than those for typhoid, although this was controverted by Ninomiya.²³¹ Heuer believed the bacteriolysins less resistant than the agglutinins. Brawn²³² found ultraviolet light to destroy complement but to have no effect on cholesterolized antigen or on Wassermann negative or positive human serums. Gordon and Wormall²³³ found that the destruction of serum complement is not due to oxidation, although the rate of inactivation appeared to be slightly less in a vacuum than in air. It is the heat-labile protein component that is most affected. Levine²³⁴ attributes the destruction to the coagulation of certain protein components.

²²⁴ Brotzu, G., *Boll. soc. ital. biol. sper.*, 8, 1722 (1933); *Chem. Abs.*, 28, 4470 (1934).

²²⁵ Diacono, H., *Arch. Inst. Pasteur Tunis*, 20, 48 (1931); *Chem. Abs.*, 25, 4312 (1931).

²²⁶ Marras, F. M., and Omar, W., *J. Egyptian Med. Assoc.*, 17, 687 (1934); *Chem. Abs.*, 28, 7288 (1934).

²²⁷ Kallós, P., and Kallós-Deffner, L., *Klin. Wochschr.*, 14, 392 (1935); *Chem. Abs.*, 30, 3058 (1936).

²²⁸ Kitamura, S., and Murayama, M., *Klin. Wochschr.*, 16, 88 (1937); *Chem. Abs.*, 31, 3555 (1937).

²²⁹ Dujarric de la Rivière, R., and Kossovitch, N., *Ann. inst. Pasteur*, 55, 331 (1935); *Chem. Abs.*, 30, 4206 (1936).

²³⁰ Heuer, G., *Centralbl. Bakt. Parasitenk.*, I, 88, 380 (1922).

²³¹ Ninomiya, R., *Z. Immunitäts.*, 39, 494 (1924); *Chem. Abs.*, 18, 2555 (1924).

²³² Brawn, G., *Z. Immunitäts.*, 44, 27 (1925); *Chem. Abs.*, 20, 1267 (1926). See also Bovie, W. T., *J. Med. Research*, 38, 335 (1918).

²³³ Gordon, J., and Wormall, A., *Biochem. J.*, 22, 909 (1928).

²³⁴ Levine, B. S., *Am. Med.*, 35, 610 (1929); *Chem. Abs.*, 24, 2174 (1930). See also Friedberger, E., and Scimone, V., *Z. Immunitäts.*, 37, 341 (1923); *Chem. Abs.*, 18, 551 (1924).

Hassko²⁸⁵ states that complement, the antibodies in positive human serums, amboceptors, agglutinins and precipitins all lose their specific activity partly or completely under the influence of ultraviolet rays, the extent depending upon the dilution of the protein, its colloidal properties and various other conditions. Egg albumin irradiated for nine hours is non-precipitable by neocarsphenamine. Paic and Haber²⁸⁶ find the inhibiting action of mixed light on complement to be appreciable after thirty minutes of irradiation. Destruction is complete after ten hours. Petterson²⁸⁷ maintains that ultraviolet rays are more active than visible light in inactivating *in vitro* the bactericidal substances of the body. Serum alexin is much more sensitive than β -lysin and the bactericidal substances of white blood cells. Active β -lysin is as sensitive as the inactivated substance. Blanchard²⁸⁸ finds the opsonic activity of normal cat serum decreased on exposure to a mercury-arc lamp. He suggests that irradiation inactivates the opsonins, which are probably protein-like, by changing their colloidal state.

Growth. Studies have been made of the effect of daily irradiations of animals upon their growth. Leigh-Clare²⁸⁹ found that, if their eyes were shielded, exposures of young growing rats for periods up to thirty minutes daily had no deleterious effect. Suzuki and Hatano²⁹⁰ concluded from a series of experiments with white rats, chickens and rabbits, that the ultraviolet rays present in ordinary daylight are far from sufficient for the vigorous development of young chicks.

The rate of growth or the histological anatomy of the thyroid gland of rats is unaffected by daylight, darkness or ultraviolet light environments during their growth, according to Mayerson.²⁴¹

Tadpoles receiving dried milk from thyroidectomized, nonirradiated goats were found by Kucera and Soos²⁴² to grow slowly and develop abnormally small thyroids. If the udder of the thyroidectomized goat was irradiated, the retarding effect of the milk on the tadpoles was decreased, but they did not develop as fast as those receiving milk from normal goats. The milk from irradiated thyroidectomized goats receiving potassium iodide permitted more rapid development. Rats kept in darkness have an average blood iodine of 25 γ per cent. In the dried thyroid gland there is 211 γ per cent.²⁴³ The gland has the histological picture of increased activity, that is, less colloid, an increased number of follicles and high irregular epithelial cells. Rats given Vigantol or ultraviolet irradiation have a high blood iodine (30 to 40 γ per cent), a low thyroid iodine content (112-167 γ per cent) and the histologic picture of increased colloid and flat, resting epithelium.²⁴⁴

Effects on the Secretory Activity of Glands. Doses of ultraviolet light strong enough to cause a rapid erythema exert a histamine-like effect upon gastric secretions, causing the appearance of free hydrochloric acid in patients with so-called histamine achylia, according to Diehl.²⁴⁵ Sunbaths are also said to stimu-

²⁸⁵ Hassko, S., *Biochem. Z.*, **226**, 462 (1930).

²⁸⁶ Paic, M., and Haber, P., *Compt. rend.*, **198**, 613 (1934).

²⁸⁷ Petterson, A., *Z. Immunitat.*, **75**, 156 (1932); *Chem. Abs.*, **26**, 5646 (1932).

²⁸⁸ Blanchard, E. W., *Physiol. Zöbl.*, **4**, 316 (1931); *Chem. Abs.*, **25**, 4599 (1931).

²⁸⁹ Leigh-Clare, J. L., *Biochem. J.*, **21**, 208 (1927).

²⁹⁰ Suzuki, K., and Hatano, T., *Bull. Agr. Chem. Soc. Japan*, **3**, 14; *Chem. Abs.*, **22**, 1182 (1928).

²⁴¹ Mayerson, H. S., *Am. J. Physiol.*, **113**, 659 (1935). See, however, Bennholdt-Thomsen and Ziegler-Wellmann.²⁴³

²⁴² Kucera, C., and Soos, M., *Compt. rend. soc. biol.*, **113**, 619 (1933); Andrik, L., and Kucera, C., *Ibid.*, **622**; *Chem. Abs.*, **27**, 4564 (1933).

²⁴³ Bennholdt-Thomsen, C., and Ziegler-Wellmann, M., *Klin. Wochschr.*, **13**, 800 (1934); *Chem. Abs.*, **28**, 6734 (1934).

²⁴⁴ For the effect of ultraviolet rays on lymphoid tissue, see Jolly, J., *Compt. rend. soc. biol.*, **93**, 999 (1925).

²⁴⁵ Diehl, F., *Arch. exp'tl. Path. Pharmacol.*, **159**, 367 (1931).

late gastric secretion.²⁴⁶ The usual daily variations in the acidity of the gastric juice are, however, so great as to make definite conclusions somewhat uncertain.²⁴⁷ Considerable decreases in the secretory activity of the pancreas occur from three to five hours after fifteen to thirty minutes of irradiation of dogs.²⁴⁸ With shorter irradiation periods (seven minutes) the effects were variable. The effect is attributed to a substance brought to the gland by the blood and produced originally by the irradiation.

Gedda²⁴⁹ finds a fifteen-minute irradiation of human subjects to have a diuretic effect, increasing not only the volume of urine but also its content of urea and especially of chlorides.

Light treatment particularly by visible rays, increases the accumulation of zinc²⁵⁰ in the tissues of animals to which the metal is administered over that of animals receiving the same amount but not irradiated. Pincussen has discussed²⁵¹ the acceleration of the excretion of lead brought about by irradiation. Pincussen and Roman²⁵² demonstrated that irradiation by the mercury arc increases the ratio of organic to inorganic iodine in both normal and dye-injected mice. It also increases the organic bromine at the expense of the inorganic bromine but has no similar effect upon the distribution of chlorine.

A number of experiments have been made upon portions of non-intact animals. Azuma and Hill²⁵³ found irradiation of involuntary muscle by ultraviolet rays antagonized the action of adrenalin but not that of emetine. These rays increase the tone and rhythmic contractions of the muscle of the frog rectum if there is calcium in the nutrient fluid employed.²⁵⁴ In the presence of magnesium, however, they cause relaxation and cessation of rhythmic contractions. The presence of calcium ions is also necessary for ultraviolet rays to stimulate the contraction of skeletal muscle suspended in Tyrode's solution. Potassium and magnesium ions appeared to moderate the effect of the calcium ions.²⁵⁵

Petersson²⁵⁶ believes ultraviolet light weakens the parasympathetic excitability of the surviving intestine and uterus by diminishing the excitability of the sympathetic inhibitor and increasing that of the sympathetic motor. These modifications of excitability are thought to be durable and to persist after the cessation of the irradiation.

Ultraviolet light directly stimulates the contracture of skeletal muscle of the frog independently of the presence of molecular oxygen.²⁵⁷ The redox potential is increased, the maximum effect being produced by ten minutes of irradiation.²⁵⁸ Larger doses inhibit the change. The effect is produced immediately after the exposure to ultraviolet rays. For the effect to occur, the dehydrogenase and hydrogen donor system must be present. At an optimum dosage, the reduced glutathione increases, the reverse occurring when excessive doses are used. Ashkenaz finds stimulation by ultraviolet light causes muscle fibers to give off calcium.²⁵⁹

It has been shown by Kler²⁶⁰ that under suitable conditions, ultraviolet rays stimulate a rhythmic contraction of the heart *in vitro*. The cardiac effects of atropine are also influenced by irradiation of a human subject to whom it is administered, according to

²⁴⁶ Barone, V. G., *Arch. Fisiol.*, **31**, 468 (1932); *Chem. Abs.*, **27**, 1667 (1933).

²⁴⁷ Keller, P., and Loeb, M., *Klin. Wochschr.*, **4**, 2390 (1925); *Chem. Abs.*, **20**, 922 (1926).

²⁴⁸ Glikson, E. B., *Arch. sci. biol. (U.S.S.R.)*, **39**, 629 (1935); *Chem. Abs.*, **30**, 6023 (1936).

²⁴⁹ Gedda, L., *Minerva Med.*, **1**, 841 (1933); *Chem. Abs.*, **27**, 4300 (1933).

²⁵⁰ Nakadate, K., *Biochem. Z.*, **265**, 61 (1933).

²⁵¹ Pincussen, L., *Klin. Wochschr.*, **12**, 275 (1933).

²⁵² Pincussen, L., and Roman, W., *Biochem. Z.*, **216**, 3336 (1929).

²⁵³ Azuma, Y., and Hill, L., *Proc. Roy. Soc.*, **99B**, 221 (1926).

²⁵⁴ Azuma, Y., *Proc. Roy. Soc.*, **100B**, 431 (1926).

²⁵⁵ Azuma, Y., *Proc. Roy. Soc.*, **101B**, 24 (1927).

²⁵⁶ Petersson, F., *Compt. rend. soc. biol.*, **99**, 1677 (1928); *Chem. Abs.*, **23**, 622 (1929).

²⁵⁷ Speakman, C. R., and Blum, H. F., *J. Cellular Comp. Physiol.*, **3**, 397 (1933).

²⁵⁸ Uchimura, T., *J. Biochem. (Japan)*, **25**, 207 (1937); *Chem. Abs.*, **31**, 5395 (1937).

²⁵⁹ Ashkenaz, E. W., *J. Cellular Comp. Physiol.*, **12**, 139 (1938); *Chem. Abs.*, **32**, 9112 (1938).

²⁶⁰ Kler, S., *Compt. rend. soc. biol.*, **93**, 1391 (1925); *Chem. Abs.*, **20**, 1821 (1926); see also Wastl, H., *Arch. expil. Path. Pharmacol.*, **114**, 56 (1926).

Garot.²⁶¹ When administered immediately after the irradiation of children it causes an acceleration of the pulse rate more rapidly but less marked than in the case of non-irradiated subjects.

A substance present in alcoholic extracts of skeletal muscle which stimulates the action of the isolated toad heart is not affected by irradiation, according to Oana.²⁶² Haberlandt²⁶³ believes the stimulating substance which may be extracted from the heart of the frog in Ringer's solution can be partly, but not completely, destroyed by ultraviolet light. In this respect he thought it to resemble adrenaline and the accelerating substance of Loewi.

Offant and Dubouloz²⁶⁴ claimed that the rhythm of the perfused frog heart can be affected by the use of irradiated Ringer's solution as the perfusion fluid, unless the solution had been kept at 100° during irradiation. Renosto,²⁶⁵ however, found that, in the absence of sensitizers, ultraviolet irradiation of either the heart itself or the perfusion fluid had no effect. In the presence of dyestuffs in the perfusion liquid there could be observed, after a latent period following irradiation, a lessened amplitude of the contractions of the heart without any change in the tone, rhythm or frequency.

Recently, Guttman²⁶⁶ found that after the rhythm of frog or *Limulus* hearts had been stopped by the addition of an excess of potassium to the perfusion fluid, it could be promptly restored by ultraviolet irradiation. He also noted²⁶⁷ that irradiation of the clam heart in sea water for two or three minutes caused a marked increase in tonus and a definite decrease in amplitude, but that the pace-maker was not affected. It was suggested that irradiation may increase the permeability of the cells, permitting potassium to leave and calcium to enter. The rate of the *Limulus* heart in sea water was increased by ultraviolet irradiation. The same effect was observed when the heart was shielded from the rays and masses of skeletal or smooth muscle were irradiated instead. This was explained by the assumption of the production of an accelerator substance in these tissues which diffuses to the heart. About twenty minutes after the cessation of the irradiation, the frequency and amplitude are diminished, possibly because of the formation of a depressor substance.²⁶⁸

Milk. In women, ultraviolet irradiation appeared to increase the quantity of milk secreted in ten of fifteen cases studied by Lesné and Dreyfus-Sée.²⁶⁹ Aside from an increase in the antirachitic properties of the milk, its chemical composition was unaffected. Knott and Garver²⁷⁰ found that irradiation of the udders of cows for twenty minutes daily for 21 days had no significant effect upon the quantity of milk produced or on the content of its butter fat or total solids.

Martini²⁷¹ finds the milk of various species of animals to exhibit different powers of reducing methylene blue in light. The most active is that of sheep. Cows' milk loses this power very easily, especially if exposed to light. The property is ascribed, not to the fatty components of the milk, but rather to a thermostable, water-soluble substance, possibly glutathione.

The oxidation-reduction potentials of cream and whole or skimmed milk drift toward the negative side on exposure to light.²⁷² This potential change is accentuated by the addition of methylene blue. As the solutions develop a progressively more negative potential, methylene blue becomes decolorized when this potential

²⁶¹ Garot, L., *Compt. rend. soc. biol.*, **96**, 1048 (1927); *Chem. Abs.*, **21**, 2333 (1927).

²⁶² Oana, M., *Japan. J. Exptl. Med.*, **10**, 123 (1932); *Chem. Abs.*, **26**, 4852 (1932).

²⁶³ Haberlandt, L., *Arch. ges. Physiol.*, (*Pflüger's*), **218**, 129 (1927); *Klin. Wochschr.*, **6**, 2099 (1927).

²⁶⁴ Offant, C., and Dubouloz, P., *Compt. rend. soc. biol.*, **112**, 373 (1933); **115**, 1300 (1934); *Chem. Abs.*, **28**, 4479 (1934).

²⁶⁵ Renosto, G., *Boll. soc. ital. biol. sper.*, **10**, 295 (1935); *Chem. Abs.*, **29**, 6308 (1935).

²⁶⁶ Guttman, S. A., *J. Cellular Comparative Physiol.*, **8**, 37 (1936); *Chem. Abs.*, **30**, 5662 (1936).

²⁶⁷ Guttman, S. A., *Proc. Soc. Exptl. Biol. Med.*, **33**, 363 (1935); *Chem. Abs.*, **30**, 8250 (1936).

²⁶⁸ Guttman, S. A., *Biol. Bull.*, **72**, 75 (1937).

²⁶⁹ Lesné, E., and Dreyfus-Sée, G., *Lait*, **11**, 155 (1931); *Chem. Abs.*, **25**, 4032 (1931).

²⁷⁰ Knott, J. C., and Garver, H. L., *Ann. Report Washington Agr. Expt. Sta., Bull.* **260**, 27 (1931); *Chem. Abs.*, **26**, 4615 (1932).

²⁷¹ Martini, V., *Boll. soc. ital. biol. sper.*, **6**, 773 (1931); *Chem. Abs.*, **26**, 1631 (1932).

²⁷² Aikins, G. A., and Fay, A. C., *J. Agr. Research*, **44**, 85 (1932); *Chem. Abs.*, **26**, 3045 (1932); Martini, E., *Biochem. Z.*, **260**, 153 (1933).

reaches that capable of reducing the dye. Similarly, the blue color reappears when the solution develops a potential sufficiently positive to oxidize the dye. The addition of fat to skimmed milk hastens the reduction time of methylene blue in samples exposed to sunlight, probably because of the tendency of the fat to elevate the zone of reduction. However, the reducing intensity induced by the growth of bacteria is more negative than that induced by sunlight. This indicates that the photoreduction of methylene blue in milk is a reaction distinct from that produced by bacteria. When skimmed milk containing methylene blue decolorized by sunlight is placed in darkness, the potential quickly becomes sufficiently positive to oxidize the leuco-base. Artificial light hastens the reduction of methylene blue in market milk. Light from a 75-watt electric bulb produces a potential drift in milk which differs only in degree from that observed in sunlight. Similar observations that the oxidation of fat in whole milk under the influence of sunlight causes the development of a reducing potential detected by its effect upon methylene blue or electrometrically were made by Whitehead.²⁷³

EFFECTS OF ULTRAVIOLET LIGHT UPON THE EYE MEDIA

As the sense-organ of reception of solar radiations, the retina would seem to require especial protection. It is, therefore, not surprising that the structures of the eye through which the rays must pass in order to reach the retina act as filters of potentially injurious rays. Against natural ultraviolet the cornea affords little protection, as it is transparent to rays of wave-length greater than 2950A.²⁷⁴ The vitreous and aqueous humors transmit the ultraviolet down to 3000A, according to Birch-Hirschfeld.²⁷⁵ It is the lens of the eye which is chiefly responsible for stopping ultraviolet rays from reaching the retina.

de Chardonnet²⁷⁶ used a quartz plate coated with a silver film of such a thickness as to be opaque to the visible and invisible spectrum except for the region between 3010 and 3430A. Through this plate normal eyes could not see an arc light, but eyes from which the lens had been removed in the operation for cataract could detect the movements of the arc.

In addition to its absorptive power, the lens can alter the rays by fluorescence. The fluorescence is excited by rays between 3500 and 4000A. Thus we see that no radiation of wave-length shorter than 3500 (or more probably 3800A) can reach the retina. In the later period of life, owing to yellowing of the media, the limit is pushed into the most refrangible region of the visible spectrum. Opinions differ greatly as to the limit of visibility. Some claim to have seen the line in the tin spectrum at 3175A.²⁷⁷ This may possibly have been due to stray reflections in the monochromators employed. Saidman and Dufestel²⁷⁸ claim to have seen faintly a line at 3650A.²⁷⁹

Exposure of the eyes to ultraviolet rays results in inflammation, but only of the superficial structures. This effect, which has been described in Chapter 10, is

²⁷³ Whitehead, H. R., *Biochem. J.*, 25, 1647 (1931).

²⁷⁴ Martin, E. K., *Proc. Roy. Soc.*, 85, 319 (1912); Schanz, F., and Stockhausen, K., *Arch. für Ophth.*, 69, 49 (1908).

²⁷⁵ Birch-Hirschfeld, A., *Arch. für Ophth.*, 71, 573 (1909).

²⁷⁶ de Chardonnet, *Compt. rend.*, 96, 509 (1883).

²⁷⁷ Glancy, A. E., *Am. J. Physiol. Optics*, 4, 145 (1923); Graham, W. P., *J. Opt. Soc. Am.*, 6, 605 (1922).

²⁷⁸ Saidman, J., and Dufestel, L. G., *Compt. rend.*, 182, 1173 (1926).

²⁷⁹ For a very detailed study of the transmission of the various media of the eye and of the eye as a whole, see Shoji, Y., *Mitt. Med. Fak. Univ. Tokyo*, 29, 61 (1922). This is discussed in Laurens, H., "The Physiological Effects of Radiant Energy," p. 150. New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), 1933.

strictly comparable with the inflammations of the skin which are intentionally provoked as part of the routine of ultraviolet therapy. Like these, the conjunctival inflammation subsides rapidly without leaving any trace. It is rarely desirable to produce such a reaction. Verhoeff and Bell,²⁸⁰ who made elaborate studies of the reaction, conclude that conjunctivitis is caused by rays of wave-lengths shorter than 3050A.

Many studies have been made upon the lens, particularly because of the possibility of a relation to the ultraviolet rays of sunlight and the production of cataracts. Burge²⁸¹ concluded that ultraviolet rays can change cell protoplasm in such a manner that certain salts may combine with it to form a precipitate or coagulum. Abnormal amounts of sodium silicate or calcium salts in the cells of the eyelids or the cornea augment the inflammatory action of the radiations. By exposing fish, living in dilute solutions of certain salts, to ultraviolet rays, he was able to produce cataracts.

The observations of Schanz²⁸² on the lens have shown that the effect of light is to render its proteins less soluble. The frequency of lenticular opacity in diabetes suggested a series of experiments in which equal amounts of a protein solution in each of a series of quartz test tubes were irradiated in the presence of increasing amounts of acetone. The results showed that the loss of solubility of the protein is increased by the presence of acetone.

Adams²⁸³ finds that, although in patients with senile cataracts the serum calcium is appreciably higher than normal, calcium salts acting on fresh ox lenses do not cause opacity unless present in non-physiological concentrations. Nor could she find them to act as sensitizers to ultraviolet radiations as had been suggested by Burge.

All wave-lengths, including infrared, visible and ultraviolet, are said by Burge, Wickwire and Schamp²⁸⁴ to be capable of rendering the lens material electro-negative and so being effective in producing its calcification. It is difficult to explain this behavior of the longer wave-lengths physically and these authors note the shorter wave-lengths to be much the more effective. Hinrichs²⁸⁵ suggests that the effect of ultraviolet irradiation of excised lenses in 0.1- to 1-per cent solutions of sodium chloride and calcium chloride is probably a surface phenomenon. There is involved a change in the permeability to salts or their ions and a subsequent precipitation of the lens protein. Calcium is more effective than sodium in producing the lens opacity.

Opinion at present does not ascribe the origin of cataracts in glass workers to visible rays and probably not to the direct action of either the infrared rays or the ultraviolet rays. Bradford and others suggested²⁸⁶ the possibility that an indirect action on the nutrition of the lens may be ascribed to the action of the infrared rays on the iris and ciliary bodies.²⁸⁷

Lieben and Kronfeld²⁸⁸ illuminated the lenses of fresh intact pigs' eyes with diffused daylight in the presence of a sensitizer and also by a quartz lamp both

²⁸⁰ Verhoeff, F. H., and Bell, L., *Proc. Am. Acad. Arts Sci.*, 51, 640 (1916).

²⁸¹ Burge, W. E., *Am. J. Physiol.*, 39, 335 (1916).

²⁸² Schanz, F., *Arch. ges. Physiol. (Pflüger's)*, 170, 646 (1918); *J. Chem. Soc.*, 118, II, 213 (1920).

²⁸³ Adams, D. R., *Biochem. J.*, 23, 902 (1928).

²⁸⁴ Burge, W. E., Wickwire, G. C., and Schamp, H. M., *Arch. Ophthalmol.*, 17, 234 (1937); *Chem. Abs.*, 31, 3133 (1937).

²⁸⁵ Hinrichs, M., *Proc. Soc. Exptl. Biol. Med.*, 27, 535 (1930).

²⁸⁶ Report of Glass Workers' Cataract Committee, *Proc. Roy. Soc.*, 103B, 192 (1928).

²⁸⁷ Note also Sheard, C., *Am. J. Physiol. Optics*, 5, 214 (1924).

²⁸⁸ Lieben, F., and Kronfeld, P., *Biochem. Z.*, 197, 136 (1928).

with and without a sensitizer. In no case could there be observed any decrease in the tryptophane content of the lens proteins. Under the same conditions in solutions of the lenses in alkali, containing the equivalent of 0.5 per cent of protein, considerable destruction of this amino- acid occurred, but since the destruction did not occur in solutions four times as concentrated, it was assumed that the protein of the lens is protected in high concentrations from chemical changes due to light. Normal human lenses and those with cataracts showed no difference in the tryptophane content of their protein.

The ability of the lens to oxidize certain organic acids (fumaric, malic and succinic) is decreased by exposure to ultraviolet light.²⁸⁹

The glutathione content of the ox lens is decreased by exposure to ultraviolet light and to a more marked extent by heat rays. Frog eyes not exposed to light show an oxygen consumption of the order of 6.5 cu. mm. per gm. of tissue per minute. This is decreased by exposure to light.²⁹⁰

The lactic acid content of the aqueous humor is unaffected by keeping animals in light or darkness.²⁹¹ The natural vitreous humor of pH 8.2 absorbs near 2600 to 2700A, differing from the crystalline humor which absorbs at 2760A.²⁹²

EFFECTS OF ULTRAVIOLET LIGHT ON DEVELOPMENT OF SIMPLE ORGANISMS

Lillie and Baskerville²⁹³ in reporting experiments on starfish eggs, state the effects produced in unfertilized eggs by brief irradiation with ultraviolet rays to resemble those of partial activation. The immediate change produced in the egg system is of the same essential nature as that caused by temporary exposure to high temperature or other activating agent. The primary effect of the rays is probably a structural change, that is a change in the colloidal substratum of the protoplasm and probably of the surface layer, upon which follow specific chemical effects as a secondary consequence.

Exposure of the eggs of *Chaetopterus* for sixty to seventy seconds at 21.5 cm. from a mercury arc leads to a tendency of the eggs to fuse, after insemination, during the cleavage stages into masses of twelve to fifteen eggs, because of changes in the cortex.²⁹⁴

Irradiation of normal *Arbacia* eggs produces at first a slight increase, then a decrease and finally a complete loss of the power of producing fertilizin.²⁹⁵ The irradiation of normal egg water produces a fading of the echinochrome pigment, a slight increase in the pH, and a reduction of the agglutination of fertilizin. The more concentrated suspensions of sperm show an increase of viscosity and a decrease of surface tension following irradiation. Irradiated sperms show a reduction of agglutinability by normal egg water. The more dilute suspensions are the more susceptible.

Vlès and Gex²⁹⁶ found the principal absorption band of sea urchin eggs to be at about 2800A.

The growth of cultures of connective tissue may be inhibited by an eight

²⁸⁹ Adams, D., *Proc. Roy. Soc.*, **98B**, 244 (1925); *Biochem. J.*, **23**, 902 (1929).

²⁹⁰ Noyons, A., and Wiersma, C., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **3**, 156 (1933); *Chem. Abs.*, **28**, 7337 (1934).

²⁹¹ Wittgenstein, A., and Gaedertz, A., *Biochem. Z.*, **176**, 1 (1926).

²⁹² Abe, T., *Arch. phys. biol.*, **6**, 1 (1927); *Chem. Abs.*, **23**, 3499 (1929).

²⁹³ Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.*, **61**, 57 (1922); *Chem. Abs.*, **16**, 2937 (1922); cf. Baldwin, W. M., *Biol. Bull.*, **37**, 294 (1919); *Chem. Abs.*, **14**, 1164 (1920).

²⁹⁴ Just, E. E., *Science*, **71**, 72 (1930).

²⁹⁵ Hinrichs, M. A., *Biol. Bull. Marine Biol. Lab.*, **53**, 416 (1927); *Chem. Abs.*, **22**, 463 (1928).

²⁹⁶ Vlès, F., and Gex, M., *Bull. Inst. Oceanograph*, **658**, 23 pp. (1934); *Chem. Abs.*, **29**, 2184 (1935).

to ten minutes' exposure to ultraviolet rays, but the cells regain their proliferative power when transferred to a fresh medium. The lethal dose is ten to fifteen times as large.²⁹⁷

Chick embryos show a differential susceptibility to ultraviolet irradiation, the regions of greatest physiological activity being the most easily modified by sub-lethal doses.²⁹⁸ These same regions also die and disintegrate the most rapidly on the application of lethal doses. In the embryonic stages there is a single antero-posterior gradient of susceptibility which in later stages is complicated by the appearance of local regions of high susceptibility. In general, the susceptibility to the modification of development by ultraviolet irradiation is proportional to the dosage.

The effects of local ultraviolet irradiation of developing embryos of *Triton taeniatus* are largely limited to the surface cells, according to Dürken,²⁹⁹ probably on account of the great light absorption by the yolk granules. The result is a pigmentation of the irradiated area, followed by a contraction of the surface of the cell, which forces out its contents. In the later stages of development, irradiation kills the entire cell on which it falls, and the dead cell is either thrown out or, in still older embryos, remains within the organism without undergoing further development. Irradiation of the organizer region of the *Triton* embryo can completely or partially inhibit the organizing action without killing the embryo.³⁰⁰ Since the active substance appears to be very stable, its direct inactivation by light seems improbable. Reith, however, regards the power of induction by the organizer region (blastopore lip) when implanted in normal gastrulae as very resistant to ultraviolet radiations.³⁰¹

To determine the nature of the colloidal changes which occur in irradiated protoplasm, Remotti³⁰² bred some of the young of *Salmo lacustris* in darkness and exposed others to a 1000 c.p. electric light. The serum drawn from the irradiated and sectioned embryos reacted more slowly with hydroquinol than that from non-irradiated ones.

Chick embryo cells grown in media containing cancer-producing hydrocarbons are photosensitive. Methylcholanthrene, 1,2,5,6-dibenzanthrene and 1,2-benzopyrene in concentrations of 0.05 to 0.1 per cent do not affect the growth or mitosis of the cells until the cultures are exposed to a bright light. Exposures of two to ten minutes cause changes in the cells and inhibit mitosis, but the cells subsequently recover and proliferate, unless the exposures have been unduly prolonged.³⁰³

Ultraviolet irradiation of the larvae of *Drosophila melanogaster* does not prolong the larval stage as do x-rays. The immediate effects on carbon dioxide formation were, however, similar, according to Thompson.³⁰⁴ Small doses of ultraviolet light hasten the development of mosquito larvae, but larger amounts, and also complete darkness, are harmful.³⁰⁵

The penetration of acetic acid into the living larvae of frogs occurs more slowly

²⁹⁷ Kler, S., *Compt. rend. soc. biol.*, 93, 1389 (1925); *Chem. Abs.*, 20, 1821 (1926).

²⁹⁸ Hinrichs, M. A., *J. Exptl. Zööl.*, 47, 309 (1927); *Chem. Abs.*, 22, 994 (1928).

²⁹⁹ Dürken, B., *Z. wiss. Zööl.*, 144, 123 (1933); *Chem. Abs.*, 28, 534 (1934).

³⁰⁰ Dürken, B., *Z. wiss. Zööl.*, 147, 295 (1935).

³⁰¹ Reith, F., *Z. wiss. Zööl.*, 150, 179 (1937); *Chem. Abs.*, 32, 3490 (1938).

³⁰² Remotti, E., *Atti accad. Lincei*, 3, 772 (1926); *Chem. Abs.*, 20, 3196 (1926).

³⁰³ Lewis, M. R., *Am. J. Cancer*, 25, 305 (1935).

³⁰⁴ Thompson, W. R., *J. Gen. Physiol.*, 18, 869 (1935).

³⁰⁵ Frost, F. M., Herms, W. B., and Hoskins, W., *J. Exptl. Zööl.*, 73, 461 (1936); *Chem. Abs.*, 30, 8404 (1936).

in darkness than in light.⁸⁰⁶ If the larvae are exposed to ordinary light, the illumination is followed by no after-effects, but if the quartz lamp is used, a definite influence on the permeability of the larvae remains. The irradiation of tadpoles causes accelerated development, but that of frog and toad spawn is without effect.⁸⁰⁷

Higgins and Sheard⁸⁰⁸ stated in respect to the early larval development of *Rana pipiens* that the stimulative action of light is due to the region between 4000 and 2800 Å and that lethal effects are due to wave-lengths shorter than 2800 Å. Ultraviolet rays stimulate the exogenous growth of cells and of the organism as a whole. However, they inhibit subsequent exogenous metabolic processes and therefore interfere with growth and cause death.

Neoplasms. The excess of nuclein phosphorus in cancerous tissue over that in normal tissue observed by Enselse and Enselse⁸⁰⁹ disappears after ultraviolet irradiation. On the other hand, lipid phosphorus increases in the irradiated tumor at the same time as the proportion of fat. Under the influence of irradiation, the tendency is for the nuclear constituents to be decreased and for the cancerous tissue to be transformed into fat.

Strong irradiation with ordinary incandescent lamps seemed to accelerate the development of papillomas and cancers in mice treated with tar by Vlès, de Coulon and Ugo.⁸¹⁰

Lecithin, especially after irradiation with ultraviolet light for 24 to 600 hours is said by Roffo⁸¹¹ to inhibit the growth of sarcoma cells *in vitro*.

Roffo and Pilar⁸¹² called attention to a possible relation between the increased cholesterol content of skin irradiated by ultraviolet light and the formation of tumors. They observed that 92 per cent of the skin tumors of the face occurred on the parts directly exposed to the sun. Keratotic carcinomas follow hyperkeratotic injuries to the skin exposed to the sun.⁸¹³

They occur particularly in blondes; pigmented skins are more resistant to the light. All of the cases studied gave a history of long exposure to the sun and only 3.62 per cent were less than forty years of age. Roffo⁸¹⁴ exposed ten rats to ultraviolet light. Three died within a few days. The remaining rats were exposed to gradually increasing doses for two weeks and then to a continuation of the last dose for seven or eight months. All these animals developed tumors, multiple keratoses, papillomas, carcinomas and sarcomas. The common sites of the tumors were the regions naturally free from hair, such as the ear, the conjunctiva, or regions from which the hair had been removed. In one animal there was a spindle cell sarcoma on one ear and a carcinoma on the other.

On the other hand, Seel and Carls⁸¹⁵ find ultraviolet irradiation to inhibit the formation of metastases in rabbits injected with the Brown-Pierce sarcoma. It was even able to prolong their lives.

⁸⁰⁶ Van Herwerden, M. A., *Protoplasma*, 8, 413 (1929); *Chem. Abs.*, 25, 3405 (1931).

⁸⁰⁷ Abderhalden, E., and Hartmann, J., *Arch. ges. Physiol. (Pflüger's)*, 218, 261 (1927); *Chem. Abs.*, 22, 1810 (1928).

⁸⁰⁸ Higgins, G. M., and Sheard, C., *J. Exptl. Zool.*, 46, 333 (1926); *Chem. Abs.*, 21, 3236 (1927).

⁸⁰⁹ Enselse, J., and Enselse, J., *Compt. rend.*, 184, 1353 (1927).

⁸¹⁰ Vlès, F., de Coulon, A., and Ugo, A., *Arch. phys. biol.*, 12, 255 (1935); *Chem. Abs.*, 30, 1862 (1936).

⁸¹¹ Roffo, A. H., *Bol. inst. med. exptl. estudio cancer*, No. 41, 4 (1936); *Chem. Abs.*, 31, 4393 (1937).

⁸¹² Roffo, A. H., and Pilar, F., *J. Physiol. Path. Gen.*, 28, 854 (1934); *Chem. Abs.*, 25, 2478 (1931).

⁸¹³ Roffo, A. H., *Neoplasmes*, 12, 257, 521 (1933).

⁸¹⁴ Roffo, A. H., *Ibid.*, 13, 129 (1934); *Chem. Abs.*, 29, 507 (1935).

⁸¹⁵ Seel, H., and Carls, H., *Z. Krebsforschung*, 40, 416 (1934); *Chem. Abs.*, 28, 3787 (1934).

MISCELLANEOUS EFFECTS ON VARIOUS ORGANISMS

Henri and Mme. Henri³¹⁶ have shown that ultraviolet rays produce involuntary movements in small animals, that a fixed minimum exposure (initial period) is required to produce this effect, and that a definite time (latent period) elapses between the termination of the initial period and the movement. The results show that during the initial period photochemical reactions take place in the peripheral organs and that the products of these reactions are distributed by diffusion and osmosis. The initial and latent periods are not affected by change of temperature. Prolonged exposure to ultraviolet rays renders *Cyclops* immobile, but it responds to ultraviolet rays and the "initial period" is then longer, but gradually returns to its primitive value. This is also the case with an animal in which the nerve terminals have been etherized. The phenomenon of fatigue and the recovery of excitability by ultraviolet radiation, therefore, has its seat in the peripheral organs.

Hinrichs³¹⁷ maintains that the amount of irradiation in a given spectral region absorbed by the protoplasm in a given period of time determines whether there is to be an increase or a decrease in the rate of the physiological processes.

The respiration of *Calanus finmarchius* may be increased 100 per cent by light, according to Marshall, Nicholls and Orr.³¹⁸

The photolytic action of light on the luminescent granules of the ctenophore, *Euchoris multicornis*, according to Moore,³¹⁹ conforms to the Bunsen-Roscoe law; it proceeds as a first-order reaction and is not accelerated by a rise in temperature.

Recent observations by Kuhn, Moewus and Jerchel³²⁰ indicate that illumination of an aqueous suspension of the gametes of *Chlamydomonas eugametos* leads to the formation of certain substances which pass into the surrounding solution, and enable it, when added to a dark culture of gametes, to cause them to develop motile flagella and to fuse. These substances may also be destroyed by prolonged exposure of the solutions to light. The motility and development of flagella is produced by red, yellow, green, blue and total visible light, but fusion is produced only by blue and ultraviolet light. These authors have concentrated the motility substance obtained by illumination of gametes with a 500-watt lamp, obtaining it as an orange-yellow dye, which after hydrolysis yielded in chloroform a spectrum similar to that of *trans*-crocetin. The original substance may be a glucoside of crocetin, similar to the crocin of saffron. The fusion substances, different for the male and female gametes, have not yet been concentrated. The precursor is exceedingly sensitive to light. The light-transformed product is an orange-yellow, chloroform-soluble dye with properties similar to those of *trans*-crocetin dimethyl ester. The *cis* form of crocetin dimethyl ester easily rearranges to the *trans* form in blue or violet light.

The absorption spectrum of the porphyrin obtained by extracting the integument of earthworms in darkness is rather rapidly altered by irradiation with light.³²¹

Mitogenetic Radiations. In 1923, Gurwitsch³²² claimed that certain biological systems, such as the root tips of onion at certain periods of development, emit radiations in the short ultraviolet which may be detected by their ability to stimulate the growth of other tissues. These rays are called mitogenetic radiations. An extremely large

³¹⁶ Henri, V., and Henri, Mme., *Compt. rend.*, **155**, 414 (1912); *J. Chem. Soc.*, **102**, 964 (1912).

³¹⁷ Hinrichs, M., *Proc. Soc. Exptl. Med. Biol.*, **26**, 175 (1928).

³¹⁸ Marshall, S. M., Nicholls, A. G., and Orr, A. P., *J. Marine Biol. Assoc.*, **20**, 1 (1935); *Chem. Abs.*, **29**, 3045 (1935).

³¹⁹ Moore, A. R., *J. Gen. Physiol.*, **8**, 303 (1926).

³²⁰ Kuhn, R., Moewus, F., and Jerchel, D., *Ber.*, **71B**, 1541 (1938).

³²¹ Kobayashi, S., *Sci., Repts. Tohoku Imp. Univ.*, **5**, 763 (1930); *Chem. Abs.*, **25**, 2489 (1931)

³²² Gurwitsch, L., *Arch. Mikrosk. Anat. u. Entw. Mech.*, **100**, 11 (1923).

number of papers deal with this phenomenon, but as yet its existence can scarcely be said to be established. The radiations are usually stated to lie within the wave-length range of 1900 to 2500A, but to be emitted in such low intensities (about 100 quanta per sq. cm. per second) that only by the use of a Geiger counter could they be physically detected. Some competent observers using this method have failed to detect any evidence of their existence.⁵²³ Most who claim their existence have used biological systems for their detection. In view of the uncertainty which surrounds this field no further discussion will be given here of the more than six hundred recent papers concerning this alleged phenomenon. The reader is referred to the critical reviews of Hollaender and Claus.^{524, 525} It is said that the origin is one of several chemiluminescent reactions such as oxidation, glucolysis, hydrolysis, splitting of nucleic acid, etc. It has even been stated that such processes as the setting of plaster of Paris emit ultraviolet rays detectable only by their ability to produce a pigmentation of the skin. Closely related are the necrobiotic rays which Lepeschkin believes to be emitted during the decomposition of constituents of cells which have just died.⁵²⁶

⁵²³ Lorenz, E., *U. S. Public Health Repts.*, 48, 1311 (1933).

⁵²⁴ Hollaender, A., and Claus, W. D., *J. Opt. Soc. Am.*, 25, 270 (1935).

⁵²⁵ Note also the article by Hollaender, A., in Duggar, B. M., "Biological Effects of Radiation," Vol. 2, New York, McGraw-Hill Book Company, Inc., 1936.

⁵²⁶ Lepeschkin, W. W., *Ber. deut. Bot. Ges.*, 50, 367 (1932); *Chem. Abs.*, 27, 316 (1933).

Chapter 37

Therapeutic Applications of Ultraviolet Light Exclusive of Rickets

The health-promoting properties of sunlight have been recognized from the earliest times. The Egyptians treated their sick by exposing them to the sun and the Greeks and Romans had solaria. In the development of medicine, however, actinotherapy received relatively little attention until Finsen in 1893 began a systematic study of the therapeutic uses of light.

Local Therapy. His most notable results were attained in the treatment of lupus (skin tuberculosis) by the rays from a strong carbon arc. Since the source used by Finsen was relatively poor in the effective ultraviolet radiations it was necessary to make prolonged exposures with local pressure for an hour every five days over a period of about six months. The advent of the therapeutic quartz lamp with the improvements described by Kromayer (see Chapter 7) made it possible to shorten the irradiations to but a few minutes. Although Finsen attributed the results to a direct bactericidal action of the rays, it seems, however, that in many cases the bacilli may be lodged too deep for the rays to penetrate to them. Rost, Jessonek and Reyn have suggested that the effect may be indirect since it was found that areas of lupus beyond the immediately irradiated areas also showed improvement.

Dermatologists use this form of treatment for a number of skin diseases other than lupus.¹ The Council of Physical Therapy of the American Medical Association stated that ultraviolet irradiation may produce a favorable effect in the following dermatoses: scrofuloderma, erythema induratum, eczema, psoriasis, parapsoriasis, pustular folliculitis, indolent ulcers, furunculosis, acne vulgaris, angioma serpiginosum, pityriasis rosea. It also is stated that this treatment may induce an attack, cause an exacerbation or produce other injurious effects in the following conditions: eczema, psoriasis, lupus erythematosus, herpes simplex, xeroderma pigmentosum, farmers' skin, and prematurely senile skin. It was held that in some cases the effect of the treatment may be due to a local lethal action upon the superficial diseased cells, which subsequently gradually slough off. In other cases, the effects are due to causes far more complex and as yet but little understood.²

Dentists have stated that unfiltered rays from a Kromayer lamp may be employed to advantage in the treatment of sockets after extraction to relieve pain and to promote the formation of new tissue. The usual technique is to precede a one-half to five-minute application of the rays by a thirty-minute application of infrared rays.

Sunlight therapy for local diseased areas was introduced by Bernhard in Switzerland. He states³ that he first observed the beneficial effects of sunlight

¹ Russell, W. K., *Am. Med.*, 34, 390 (1928).

² American Medical Association, "Handbook of Physical Therapy," 2nd Ed., 1937.

³ Bernhard, O., cited by Laurens, H., "The Physiological Effects of Radiant Energy," p. 136, New York, The Chemical Catalog Co. (Reinhold Publishing Corp.), 1933.

upon large intractable wounds in 1902. Bernhard attributed the beneficial effects of sunlight to the entire spectrum rather than to just the ultraviolet region. He considered the more penetrating visible and near infrared radiations to stimulate epithelization. The hyperthermia produced by the infrared rays lessens the pain and increases the local circulation. The direct application of the rays of the quartz mercury-arc lamp to wounds not only fails to provide these beneficial radiations but may be deleterious.

Rasero⁴ however, claimed that good results followed the irradiation of torpid wounds with the mercury arc, and Coulter and Smith found doses of ultraviolet light which produce a mild erythema on normal skin to aid in the treatment of burns and wounds.⁵ They also recommend ultraviolet light in the preparation of infected granulation tissue for skin grafting.

Since the water-cooled Kromayer arc emits a large proportion of its energy as wave-lengths shorter than 3000A, it tends to produce more lethal effects than the air-cooled mercury-arc. The radiations from the water-cooled arc described in Chapter 7 may be applied to areas within the body orifices by means of quartz applicators employing the principle of internal reflections. A wide variety of these, vaginal, prostatic, proctoscopic, nasal, sinus and the like, are available.

General Body Therapy. A more recent development is the general irradiation of large surfaces of the body. Among the most brilliant clinical developments of the past few decades have been those reported by Rollier and others on the use of sunlight in the treatment of tuberculosis of the bones and joints. Since these results were obtained in a clinic opened in 1903 at Leysin in the Alps, at an altitude of 1500 meters, they were attributed to the ultraviolet energy abundant in the solar radiations at those altitudes. As yet, however, there can scarcely be said to be general agreement among those who use the methods of heliotherapy most successfully as to which rays of the sunlight are of the greatest value. The problem is obviously complicated, since factors other than sunlight, such as the effects of altitude, fresh air, rest, adequate diet and other therapeutic measures affect the results attained. Thus it is difficult even to evaluate the part in the cure played by sunlight. There is obviously still a need for much experimental work before it will be known which wave-length regions contribute most to the value of this form of therapy.

That heliotherapy can be successfully employed at sea level has subsequently been demonstrated, notably by Sir Henry Gauvain in England. Gauvain attributed much of the value of heliotherapy at sea level to the frequent variations in intensity which are encountered there. It may be recalled that it had been demonstrated by Laurens and Mayerson that fluctuations in light intensity stimulate various physiological processes. Other successful clinics for heliotherapy at low altitudes have been those of Kisch near Berlin, of Phelps in New Haven at Yale,⁶ of LoGrasso at Perrysburg, New York,⁷ and one at Chestnut Hills in Pennsylvania, described by Eliason.⁸

At some of these clinics, heliotherapy has been supplemented by the use of artificial light sources, particularly during dark seasons and during the months when the ultraviolet radiations in sunlight are reduced in amount. Reyn supplemented the local treatment of lupus at the Finsen Institute with general body irradiations with

⁴ Rasero, R., *Riforma Medica Naples*, 38, 772 (1922).

⁵ Coulter, J. S., and Smith, E. M., Jr., *Radiology*, 16, 737 (1931).

⁶ Phelps, W. M., *J. Bone Joint Surgery*, 12, 253 (1930).

⁷ Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

⁸ Eliason, R. T., *Annals of Surgery*, 88, 947 (1928); note also Armand-Delille, P., *J. State Med.*, 43, 709 (1935).

the carbon arc. Others employ the air-cooled quartz mercury arc for this purpose. Mayer has, for example, stated that peritoneal tuberculosis usually responds to the latter form of treatment. The lethal rays emitted by the mercury arc are reduced considerably in intensity as compared with those of the closely applied water-cooled arc, by the greater distance between the arc and the patient. The present tendency, however, seems toward the use of the carbon arc in solaria for the irradiation of large numbers of patients at one time, since its emission corresponds so much more closely to that of sunlight than does that of the mercury arc. A recent hospital installation is shown in Figure 24 (p. 63).

Because of selective reflection of various spectral regions, consideration must be given to the nature of the reflectors used with either the carbon or the mercury arc. These, if improperly chosen, may alter the quality of the radiant energy emitted by the source. If it is desired to study the relative effectiveness of various spectral regions, provision must be made for the use of suitable filters surrounding the source to isolate various bands of wave lengths.

The intensity on a given skin surface normal to the rays varies approximately as the inverse square of the distance from the arc. This is only a rough statement because the arcs used are not true point-sources of light. The intensity also varies with the cosine of the angle made by the skin surface with the beam of radiant energy. These factors may be considered in calculating the amounts of energy received per square cm. of skin from known values of the energy output of the source under the conditions of operation employed. In practice, however, the energy incident upon the patient may be directly measured by some calibrated apparatus, such as a thermocouple, photoelectric cell, or chemical actinometer.

In determining the dosage in practical therapy, the physician is usually guided, not so much by energy measurements, as by experience with the effects of the source on patients with various types of skin. A test exposure is made to determine the time required to produce a given degree of erythema, and on this is based the dosage to be applied to the body. The erythema test is made on the patient's upper arm, which is covered by a shield cut from a large envelope and containing five small holes. Under this shield is placed a strip of the same material as the shield, which may be withdrawn so as to expose successive areas. A convenient series of exposures permits the irradiation of the areas for times successively doubled from fifteen seconds in the last exposed area to a total of four minutes in the first. These periods are usually suitable for exposures at 36 inches from a bare A-2 National Carbon Co. carbon arc with high-intensity carbons and without a filter glass. In an individual of less than average susceptibility to sunburn, the spot receiving the four-minute exposure shows a visible degree of erythema about forty minutes after the completion of the test and all five spots are clearly visible in less than two hours. Substantial pigmentation results from all exposures but that of fifteen seconds. With the filter glass in place the exposure period required to produce a given degree of erythema is three to four times as long as that required when the same carbons are used without the filter. This method of grading the dosage serves as a safeguard against overexposing areas large enough to cause painful and possibly injurious burns.

The full line curves of Figure 21 (p. 61) show the distance at which the radiation intensity in the wave-length region 2900 to 3100A. equals that found in average clinical sunlight for patients at various distances and angles from the filtered carbon arc. The average intensity of that wave-length band in clinical sunlight is taken as 14.5 microwatts per sq. cm. The curves are for high-intensity Sunshine carbons. With high-intensity therapeutic "C" carbons, the intensity will

be over three times the value indicated in the figure. With the filter removed, the intensity of radiations shorter than 3100A will be about 18 times the values shown. The wave-length range specified was chosen for reasons which will become apparent in the discussion of the treatment of rickets in the following chapter.

Several clinicians attempt, in administering general irradiations for systemic effects, to produce a gradual deep tanning of the entire body without causing vesication or undue peeling of the skin. It is scarcely necessary to state that the eyes should be carefully protected during the exposures. Details of the technic should be sought in the detailed reports in the medical literature. It is sound practice to commence by fractional exposures, at each sitting exposing a fresh part and increasing the exposure of previously irradiated regions until the irradiations cover the whole body. This has been the practice of Rollier in heliotherapy, and it finds experimental justification in the work of Levy (1916) and of Gassul (1920), who have shown that general irradiation of the whole body at the first sitting may lead to unfortunate results. Although at one time it was suggested that patients could be sensitized to light to make the treatments more effective by the injection of eosin, such methods are no longer employed.⁹

MacCormac and McCrae¹⁰ have given an account of a serious dermatitis which followed a mercury-arc irradiation of about an hour and ten minutes in the case of a patient who fell asleep during his customary artificial sunbath. After a severe sunburn, there resulted ten days later a severe toxic generalized dermatitis and recovery was delayed for over a month.

There is as yet no general agreement as to the best methods of conducting irradiation therapy. Details of the methods employed and of the results obtained in the treatment of tuberculosis of the bones and joints, peritoneum, intestines, lymph-nodes and genito-urinary system must be sought in the texts of Rollier,¹¹ of Mayer,¹² and of Russell and Russell,¹³ which deal with the experience with this therapy in France, the United States and in England.¹⁴

There has been one group of workers which holds that pigmentation is necessary to the curative action of ultraviolet rays and that its degree may be regarded as an index of the progress of the cure. A filtering action of the pigment might serve to lessen the lethal action of exposures to intense sunlight at high altitudes where there may be available a very narrow band of radiations of wave-lengths between 2970 and 2910A. However, since most of the pigment is located in the basal cells of the epithelium, and the lethal action occurs in the prickle cells, the pigment could be expected to exert a protective action only upon the deeper tissues which, except in the case of the most intense irradiations, are comparatively slightly affected.

Balderrey and Ewald¹⁵ stated that pigmentation is not merely a protection against the harmful effects of the shortest wave-lengths, but is an important factor

⁹ György, P., and Gottlieb, K., *Klin. Wochschr.*, 2, 1302 (1923); *Chem. Abs.*, 19, 1600 (1925).

¹⁰ MacCormac, H., and McCrae, H. M., *British Med. J.*, 1, 693 (1925)

¹¹ Rollier, A., "Heliotherapy." Translated by de Swietochowski, H. Milford, Oxford University Press, 1927.

¹² Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

¹³ Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1928.

¹⁴ For more recent reports, see Petter, C. K., *Ann. Internal Med.*, 4, 1452 (1931); Lehman, A. M., and Bartholomew, D. C., *J. Am. Med. Assoc.*, 98, 1343 (1932); Willis, H. S., and Cohen, J., *Am. Rev. Tuberculosis*, 23, 286 (1931); Jessel, G., *Lancet*, 1, 1182 (1931); Pardee, K., *J. Bone & Joint Surgery*, 12, 270 (1930); Cox, G. L., *Brit. J. Tuberculosis*, 24, 1 (1930); *Tubercle*, 12, 17 (1930); Phelps, W. M., *J. Bone and Joint Surgery*, 12, 253 (1930); Mayer, E., *Ann. Internal Med.*, 11, 1856 (1938).

¹⁵ Balderrey, F. C., and Ewald, E., *Am. Rev. Tuberculosis*, 8, 501 (1924).

in aiding the absorption of visible light, since its presence lessens the reflection from the skin. It also was suggested that the pigmented surface radiates heat at a slightly increased rate and so permits the body to be subjected to longer periods of irradiation without the production of symptoms of insolation.

One school maintains that pigmentation may be produced without visible erythema, provided very carefully graduated doses are employed. Another believes that in the treatment of tuberculosis, doses causing erythema are more productive of beneficial results than are repeated smaller ones. If the views of those who believe the beneficial effects are to be ascribed to the non-specific proteins or protein decomposition products produced by injured cells are held correct, it might be thought necessary to use wave-lengths capable¹⁶ of producing erythema in order to produce the necessary cell injury. If, on the other hand, the beneficial results are due to the formation in the skin of some substance with curative properties, as has from time to time been suggested in analogy with the mechanism of the cure of rickets, then it is conceivable that wave-lengths other than those which cause erythema might suffice. These speculations state problems for the future which will probably best find their solution in well-controlled experiments in large institutions. It would be possible from such experiments to learn definitely which wave-lengths are essential to the curative process and to determine with some degree of accuracy the dosages of energy required at these wave-lengths. Such information would provide a basis for a study of the mechanism by which the therapeutic results are attained—a mechanism regarding which we have at present little more than speculations.

Phelps¹⁷ has asserted that the beneficial results are due to a band of radiant energy lying between 3200 and 3800Å. His work could not, however, be corroborated by Luce-Clausen and Bayne-Jones¹⁸ and it has been suggested that his assumption that the sunlight he employed was devoid of rays shorter than 3130Å may have been erroneous and that the filters he employed in other experiments may not have completely eliminated the shorter wave-lengths.

Experiments in which guinea pigs were injected intra-abdominally with tubercle bacilli failed in most cases to indicate that irradiated animals were more resistant than the non-irradiated controls.¹⁹ Greenfield²⁰ found some favorable response in the case of irradiations by direct sunlight in such experiments.

The possibility that the production of vitamin D has a favorable effect on tuberculosis will be considered in the following chapters. As yet opinions are divergent as to the advisability of employing this form of therapy in pulmonary tuberculosis. There is still an opinion held by such workers as Rollier and many others that phototherapy is dangerous in such cases. On the other hand, several recent observers including Potter, Eberson, Cooper and others believe that if caution is used, the treatment may be productive of valuable results.

Jemma²¹ states that in twenty children with bone and joint tuberculosis, a lowered alkaline reserve was restored to normal during ultraviolet light therapy. In adult patients, Spence²² observed a considerable rise in the blood cholesterol after a month of treatment. The greatest rise occurred in those patients who

¹⁶ Peskind, S., *cf.* "Photochemical Immunization: Autogenous Vaccination Through Irradiation," S. P. Mount & Co., Cleveland, 1934.

¹⁷ Phelps, W. M., *J. Bone and Joint Surgery*, 12, 253 (1930).

¹⁸ Luce-Clausen, E. M., and Bayne-Jones, S., *Am. Review Tuberculosis*, 24, 686 (1931).

¹⁹ Steinbach, M. M., Hess, A. F., and Weinstock, M., *Am. Rev. Tuberculosis*, 22, 35 (1931).

²⁰ Greenfield, M., *Am. Rev. Tuberculosis*, 24, 695 (1931).

²¹ Jemma, G., *Pediatrica Revista*, 36, 878 (1928); *Chem. Abs.*, 22, 4620 (1928).

²² Spence, C., *Brit. J. Actinotherapy*, 3, 148 (1928); *Chem. Abs.*, 23, 858 (1929).

showed clinically the greatest improvement. No significant changes in the calcium and phosphorus levels were observed.

With the demonstration of the value of ultraviolet therapy in the treatment of tuberculosis and of rickets (see Chapter 38), irradiation came to be used with varying results in a wide variety of diseases. The literature is replete with claims for its efficacy in conditions ranging from mental diseases through whooping cough to bronchial asthma. Unfortunately, the results obtained have not been such as to sustain the enthusiasm with which the method was lauded. Illogical attempts to utilize ultraviolet light for conditions for which there is little theoretical or experimental foundation met with failure and caused many physicians to discard expensive equipment.

The physiological studies reviewed in the preceding chapter reveal few responses to ultraviolet light which may serve as a basis upon which to build a rational therapy. Studies of the irradiation of abnormal or diseased subjects have given, at least in the case of rickets, more promising results. It might be thought that the reduction in blood pressure to which reference has been made in the preceding chapter might serve as a basis for expecting irradiation to give results in the treatment of hypertension. Indeed, some favorable responses to this treatment were recorded by Laurens in a study of a series of cases of essential hypertension. Others, however, proved entirely refractory. Marx²³ reported rather favorable results in a series of 21 ambulant, hypertension patients, using carbon filament lamps. With the carbon arc, Bach²⁴ found that in 105 observations on 19 men and 10 women, the blood pressure fell during irradiation in 101, showed no change in 2 and increased slightly in 2 observations. The decreases averaged 7.2 mm; the largest was 17 mm. With the quartz mercury arc, Koenigsfeld²⁵ observed decreases of from two to eight mm. immediately after irradiation. In eclampsia, Hohenbichler²⁶ obtained marked decreases in blood pressure, but frequently it rose again shortly after the treatment. The probability is that dilatation of the skin vessels produces a transient lowering of the blood pressure and causes some decongestion of blood from the internal organs.

The results in anemias have not in general been encouraging, although some favorable results in pernicious anemia were reported from the Taft Heliotherapy Ward at the Cincinnati General Hospital.²⁷

There is a widespread impression that the employment of ultraviolet light in treating patients with diabetes is dangerous. This is in part based upon observation by Sampson²⁸ and by McCaskey.²⁹ From the fact, however, that the blood sugar is commonly reduced somewhat during irradiation, it seems that there is little if any foundation for this contention. Indeed, some workers, such as Faber and Bloch,³⁰ have obtained encouraging results in its use in the treatment of diabetic children. Grayzel, Collens and McKenzie³¹ found it to have no effect on the sugar balance of such patients.

That ultraviolet irradiation should increase the resistance of the skin to infection was a natural suggestion from the results of local therapy. Rollier noted that

²³ Marx, H., *Klin. Wochschr.*, 7, 795 (1928).

²⁴ Bach, H., *Deut. Med. Wochschr.*, 37, 401 (1911).

²⁵ Koenigsfeld, H., *Z. Klin. Med.*, 91, 159 (1921).

²⁶ Hohenbichler, A., *Centralbl. Gynäkol.*, 51, 1649 (1927).

²⁷ Friedlander, A., and Wiedemer, C., *Arch. Internal Med.*, 44, 209 (1929).

²⁸ Sampson, C. M., "Physiotherapy Technique," C. V. Mosby, St. Louis, 1923.

²⁹ McCaskey, D., *New York Med. J.*, 109, 504 (1919).

³⁰ Faber, F., and Bloch, C. E., *Am. J. Diseases of Children*, 30, 504 (1925).

³¹ Grayzel, H. G., Collens, W. S., and McKenzie, M. R., *Am. J. Diseases of Children*, 38, 513 (1929).

the eruptions of chicken pox are slighter than usual in patients with pigmented skin. Hyde and LoGrasso found that skin infections occurred but rarely in pigmented patients, and Carnot, Camus and Bepard found that in rabbits irradiated before inoculation with vaccine virus, the development of an eruption was prevented.⁸²

That the blood should also become increasingly bactericidal as a result of the generalized irradiation of a patient has been occasionally suggested. Colebrook, Eidinow and Hill⁸³ have given some evidence for a temporary increase in the bactericidal power of the blood following a single exposure to the mercury arc. Robertson⁸⁴ believed that solar or mercury-arc irradiation of rats raised their resistance to infection with *B. coli communis*. Blasi⁸⁵ found that the opsonic index of the blood serum of children with a positive von Pirquet test toward the tubercle bacillus was increased after ten irradiations with the mercury arc. Hansen found that carbon arc baths applied to 230 patients who had received single injections of dead typhoid bacilli increased the formation of agglutinins in their blood. He believed the effect due to the heat of the deeply penetrating infrared rays. In general, however, immunological experiments (described in the preceding chapter) have given little foundation for a belief that irradiation increases resistance.

Many have suggested that generalized irradiations might protect people from the common cold. Maughan and Smiley at Cornell⁸⁶ conducted a series of experiments on students, in which 23 received full mercury-arc treatments at 30 inches, the arc being operated at 4 amperes and 130 volts. The entire posterior and anterior surfaces of the body received the rays for five minutes, the treatments being given weekly for about nine weeks. 58 controls were used. During this period the number of colds per individual treated was 1.48 and per individual untreated 2.48. These workers ascribed the failure of others to reduce the incidence of colds by this method to overdoses. In a second series, in one twelve-week period the results were 1.56 and 2.80 colds in the treated and untreated subjects. A second period of nine weeks showed 1.24 and 2.79, respectively. The subjects used were selected as being especially prone to suffer colds.

These results were, however, contradicted by the work of Doull, Hardy, Clark and Herman⁸⁷ who also used mercury arcs and gave light or moderate doses which produced only a minimal erythema. The total incidence was found to be slightly higher in the irradiated patients receiving more than ten treatments than in the controls. The cases occurring in the irradiated group also appeared to be somewhat more severe than those in the non-irradiated subjects.

Barenberg, Friedman and Green,⁸⁸ found that irradiation did not protect infants from whooping cough, chicken pox or respiratory infections. Both the carbon arc and the mercury arc were used. In children the evidence from blood counts showed, according to Gonc and Kassowitz⁸⁹ no enhanced bactericidal property in the blood after ultraviolet irradiation. They concluded that in the majority of their patients, particularly if they were the hosts of an infection, daily quartz lamp

⁸² See also Rivers, T. M., Stephens, H., and Gates, F. L., *J. Exptl. Med.*, 47, 37, 45 (1928).

⁸³ Colebrook, L., Eidinow, A., and Hill, L., *Brit. J. Exptl. Path.*, 5, 54 (1924); Eidinow, A., *Lancet*, II, 963 (1927); *Med. J. and Record*, 130, 695 (1929).

⁸⁴ Robertson, E. C., *Can. Med. Assoc. J.*, 19, 154 (1928); Robertson, E. C., and Ross, J. R., *Proc. Soc. Exptl. Biol. Med.*, 27, 999 (1930).

⁸⁵ Blasi, D., *Clinica Pediatrica*, 11, 832 (1929).

⁸⁶ Maughan, G. H., and Smiley, D. E., *J. Preventive Med.*, 2, 69 (1928); *Am. J. Hygiene*, 9, 466 (1929).

⁸⁷ Doull, J. A., Hardy, M., Clark, J. H., and Herman, N. B., *Am. J. Hygiene*, 13, 460 (1931).

⁸⁸ Barenberg, L. H., Friedman, I., and Green, D., *J. Am. Med. Assoc.*, 87, 1114 (1926); Barenberg, L. H., and Lewis, J. M., *Ibid.*, 90, 504 (1928).

⁸⁹ Gonc, J. F., and Kassowitz, K., *J. Am. Med. Assoc.*, 90, 280 (1928).

irradiation led to a lowered bactericidal power of the blood. The opposite effect was obtained in a few cases. Similar observations are due to Colebrook⁴⁰ Hardy and Chapman, who studied the effect of irradiation on the ability of rabbits to resist *Bacillus leptiscpticum*, found light doses to have little effect and heavy doses to be harmful. According to Petrie,⁴¹ the susceptibility of guinea pigs to spontaneous pneumococcus infection was not affected by irradiation. Negative results were also reported by Hill, Greenwood and Topley⁴² in an extensive experiment on the effects of exposure under normal conditions on the resistance of over a thousand mice to *Pasteurella* infection.

In the annual report of the Medical Research Council of London for 1927-8, it is stated that heavy expenditures for Vita-glass or other ultraviolet-transmitting glasses for school rooms or for expensive irradiation equipment for schools has not been justified. Under the auspices of the Council, Dr. Dora Colebrook arranged an elaborate test of the value of lamp therapy, the results of which were entirely negative. Her experiment, however, has been criticized, notably by Hill and Laurie,⁴³ who felt that the control children had been unwisely selected in that they lived in a district where the hygienic conditions and the available sunlight had been adequate. Their own observations indicated that irradiation improved the appetite and sleep of a group of children. The Council on Physical Therapy of the American Medical Association has stated that as far as normal persons are concerned the claim that exposure to ultraviolet rays increases or improves the tone of the tissues or of the body as a whole, stimulates metabolism or tends to prevent colds has not been conclusively substantiated.

Thus it would seem that opinions are still divergent in regard to the value of generalized irradiations on the general health and resistance to disease. This is a particularly difficult subject to investigate objectively. General reports of feelings of exhilaration or invigoration cannot be appraised scientifically. In contrast to this, the value of irradiation on the prevention of rickets is definitely confirmed and well understood.

There is some evidence that irradiation has a beneficial effect in bronchial asthma, at least in children.⁴⁴ In hay fever, hyperesthetic rhinitis and the asthmas, investigations by Novak and Hollaender⁴⁵ indicated favorable results attributed to an influence exerted upon the blood calcium which tended to be low in these conditions. Favorable effects of ultraviolet therapy given in conjunction with calcium salts in epilepsy have been reported by Borrows.⁴⁶

Roskin and Romanova⁴⁷ find that non-therapeutic doses of novarsolan given with ultraviolet irradiations have no effect on malaria in canaries although they are effective in mice. The serum of irradiated mice has the property of increasing the therapeutic action of novarsolan, neoarsphenamine and novarsenol in the malaria of canaries, presumably because of the passive transfer of some necessary factor. Although Roskin and others claimed⁴⁸ that irradiation synergizes the trypanocidal action of neoarsphenamine, Giemsa and Ellenbogen⁴⁹ could not confirm such an action. Negative results have

⁴⁰ Colebrook, L., *Brit. Med. J.*, 2, 11 (1924).

⁴¹ Petrie, G. F., *J. Hygiene*, 30, 154 (1930-31).

⁴² Hill, L., Greenwood, M., and Topley, W., *Brit. J. Exptl. Path.*, 11, 182 (1930).

⁴³ Hill, L., and Laurie, A. R., *Lancet*, I, 182 (1931).

⁴⁴ Saidman, J., *Arch. Med. Chir. l'App. Respiratoire*, 3, 480 (1929).

⁴⁵ Novak, F. J., and Hollaender, A. R., *J. Am. Med. Assoc.*, 81, 2003 (1923); *Chem. Abs.*, 18, 1153 (1924).

⁴⁶ Borrows, P. J., *U. S. Veterans Bureau Med. Bull.*, 7, 661 (1931); *Chem. Abs.*, 26, 2245 (1932).

⁴⁷ Roskin, G., and Romanova, K., *Z. Immunitäts.*, 82, 461 (1934); *Chem. Abs.*, 28, 7361 (1934); *Z. Immunitäts.*, 62, 147, 158 (1929); 72, 445 (1931); 67, 94 (1930); *Chem. Abs.*, 25, 3080 (1931).

⁴⁸ Roskin, G., Bichowskaja, A., and Schischlaiewa, S., *Z. Immunitäts.*, 67, 91 (1930); Roskin, G., *Ibid.*, 69, 240, 473 (1930); 63, 452 (1929); *Chem. Abs.*, 25, 3080 (1931).

⁴⁹ Giemsa, G., and Ellenbogen, V., *Z. Immunitäts.*, 67, 78 (1930); *Chem. Abs.*, 25, 3080 (1931); positive results have been reported by Marzinovskii, E. J., *Z. Immunitäts.*, 74, 379 (1932) and by Orlov, S., and Levinson, L., *Ibid.*, 78, 264 (1933); *Chem. Abs.*, 27, 5422 (1933).

also been reported for the effects of ultraviolet irradiation on the splenic anemia of kala-azar by Morabito,⁵⁰ although in the anemias of luetic or tuberculous origin the results were more favorable.

Attempts have been made to treat mastitis in cows by ultraviolet irradiations; but Gildow, Hansen and Cherrington⁵¹ found no consistent reduction in the number of bacteria or of the leucocytes in the middle milk of cows with subacute or chronic mastitis after such treatment. Ultraviolet treatment has also been proposed for distemper in dogs.⁵²

Von Fellenberg⁵³ was unable to obtain evidence that ultraviolet irradiation had any effect upon endemic goiter. The weight and the iodine content of the thyroid are the same in rats reared in direct sunlight and in those reared in darkness.⁵⁴ Smith,⁵⁵ however, believes that a lack of sunlight may result in a deficiency of iodine in the thyroid gland and notes a relationship between a lack of irradiation and endemic goiter in the United States, India and New Zealand. In the last-named region the iodine content of the soil seems to be proportional to the solar radiations and similar observations have been made in regard to variations in the iodine content of potatoes grown in South Carolina.

⁵⁰ Morabito, F., *Pediatrica Revista*, **35**, 1112 (1927); *Chem. Abs.*, **22**, 1801 (1928).

⁵¹ Gildow, E. M., Hansen, H. C., and Cherrington, V. A., *J. Am. Vet. Med. Assoc.*, **35**, 55 (1933); *Chem. Abs.*, **27**, 1399 (1933).

⁵² For other applications in veterinary medicine, see Patton, J. W., *J. Am. Veterinary Med.*, **69**, 734 (1926).

⁵³ Von Fellenberg, T., *Biochem. Z.*, **235**, 205 (1935).

⁵⁴ But see Bergfeld, W., *Endokrinologie*, **6**, 269 (1930); *Chem. Abs.*, **24**, 3552 (1930).

⁵⁵ Smith, J. H., *Arch. Internal Med.*, **50**, 76 (1932).

Chapter 38

Rickets and Irradiation

Rickets is a common disease of infants and young children. It consists chiefly in a faulty deposition of calcium in the extremities of the long bones. The clinical picture is thoroughly discussed in a book by Hess¹ which also includes a critical discussion of the flood of papers which appeared subsequent to 1919 regarding the importance of vitamin D in this condition and the relation of sunlight to the production of this vitamin in the skin. The disease is accompanied by disturbances in calcium or phosphorous metabolism. It is usually characterized by low values of either or both calcium and phosphorus in the blood serum.

In 1909, the pathological studies of Schmorl² brought to light an interesting seasonal variation in the incidence of the disease. There is a high incidence of rickets in winter and the healing of the disease, slight in winter, reaches its maximum in summer. Not for some time, however, were attempts made to correlate these data with the seasonal variations of the intensity of sunlight, although it is true that an Englishman, Palm, had suggested as early as 1890³ that the chemical activity of the sun's rays may play an important part in the therapy of this disease. An experiment by Raczynski⁴ attracted little attention. He kept one puppy in sunlight and another of the same litter in darkness for six weeks. At the end of this period, the body of the first was found to contain much more calcium and phosphorus than did that of the second. Bernhard in 1917 also drew some conclusions as to the influence of sunlight on the incidence of rickets in the children of certain Alpine villages.

Apparently the first definite statement that the irradiation of a rachitic child with ultraviolet rays would bring about a cure was published by Huldshinsky in 1919.⁵ His paper contained a number of Rontgenograms which indicated beyond any doubt that the epiphyses of the long bones of rachitic infants undergo rapid calcification following the exposure of their bodies to a mercury-vapor lamp.

Clinical observations by Hess and Unger a year previously had indicated that such irradiations might have a slight effect in decreasing the size of the enlarged costo-chondral junctions, the so-called rachitic rosary, a diagnostic sign of rickets. They attached little significance to this, however, for in 1920 they stated that children in glass cubicles receiving a liberal supply of light nevertheless became rachitic and were not benefited by ultraviolet light treatments.⁶ A year later, however, they published a preliminary note on the cure of rickets by sunlight⁷ in which they employed the expression "encouraged by our results in curing rickets by means of the ultraviolet ray." At this time they also attributed the seasonal

¹ Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

² Schmorl, G., *Ergeb. der Inn. Med. u. Kinderheilk*, 4, 403 (1909); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

³ Palm, T. A., *Practitioner*, 45, 270, 321 (1890).

⁴ Raczynski, J., *Compt. rend. assoc. intern. pediat.*, 308 (1912); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

⁵ Huldshinsky, K., *Deut. Med. Wochschr.*, 45, 712 (1919).

⁶ Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.*, 74, 217 (1920).

⁷ Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.*, 77, 39 (1921)

variations in the incidence of the disease to the seasonal variations in the intensity of sunlight.⁸

The further study of this disease was promoted by the discovery that it could be produced in experimental animals by the use of deficient diets, particularly those low in phosphorus.⁹ It was soon shown that animals receiving a diet either low in phosphorus and high in calcium or one low in calcium and high in phosphorus developed symptoms of rickets. They could be protected from the effects of the diet by daily exposures to sunshine of only fifteen minutes, except in winter when longer exposures were required. The demonstration that light filtered through a window of ordinary glass was ineffective showed that only the ultraviolet portion of the solar spectrum was important. Only short periods of exposure to ultraviolet sources were required for protection against the defective diets. With the quartz mercury lamp a daily irradiation of three minutes at a distance of three feet was adequate. These effects on the growth and skeletal calcification of the rats were similar to, if not identical with, those brought about by sunshine or by the addition of cod-liver oil to the diet. Cod-liver oil was the remedy in most frequent use in the treatment of rickets.¹⁰

These results were quickly confirmed on many sides¹¹ and the curative results of carbon-arc treatments also were observed.¹² During the treatment the inorganic phosphates of the blood increased, and the signs of the disease subsided. Pre-administration of phosphates hastened the cure, although addition of dipotassium hydrogen phosphate in the absence of irradiation was unsuccessful in clinical cases.

The next important advance was the demonstration that the light acts by a chemical mechanism. Hess and Weinstock¹³ showed that a section of excised human skin after irradiation by a mercury arc when fed to rats, protected them from a deficient diet, although similar amounts of nonirradiated skin were ineffective. It was thus obvious that an antirachitic substance had been formed photochemically in the irradiated skin. This was later confirmed by Falkenheim,¹⁴ who also showed that the irradiation of but one portion of the skin of a rat produces antirachitic properties in other portions of the skin, although to a less extent than in the directly irradiated area. This observation implied that some of the active agent produced in the skin may be absorbed by the blood and distributed to other portions of the skin. As late as 1926, however, Bloch and Faber¹⁵ denied the existence of the hypothetical antirachitic material, although they admitted that ultraviolet light had a curative action on the disease. Hume, Lucas and Smith¹⁶ showed that normal calcification could be produced in rachitic rabbits by irradiating an area of skin as small as 2.5 by 3.5 cm. for only ten minutes three times a week, a proof of the extraordinary effectiveness of the unknown material formed in the skin.

It has been stated that cod-liver oil had been known for some time to contain a substance exerting a similar curative effect upon rickets and the question natu-

⁸ Hess, A. F., and Unger, L. J., *Am. J. Diseases of Children*, 22, 186 (1921).

⁹ Hess, A. F., Unger, L. J., and Pappenheimer, A. M., *J. Biol. Chem.*, 50, 77 (1922); *J. Exptl. Med.*, 36, 437 (1922); Hess, A. F., and Gutman, M. B., *J. Am. Med. Assoc.*, 78, 29 (1922).

¹⁰ Powers, G. F., Park, E. A., Shipley, P. G., McCollum, E. V., and Simmonds, N., *Proc. Soc. Exptl. Biol. Med.*, 19, 120 (1921).

¹¹ Schultzer, P., and Sonne, C., *Acta Med. Scand., Suppl.*, VII, 97 (1924); Eckstein, A., *Arch. Kinderheilk.*, 74, 1 (1924); *Chem. Abs.*, 18, 3207 (1924).

¹² Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.*, 78, 1596 (1922).

¹³ Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, 80, 687 (1922).

¹⁴ Falkenheim, C., *Klin. Wochschr.*, 5, 2071 (1926).

¹⁵ Bloch, C. E., and Faber, F., *Am. J. Diseases Children*, 30, 504 (1926).

¹⁶ Hume, E. M., Lucas, N. S., and Smith, H. H., *Biochem. J.*, 21, 362 (1927).

rally arose as to whether this might be identical with the material formed during the irradiation of skin. For several years it had been recognized, in large part because of the work of Mellanby, that cod-liver oil contains fat-soluble vitamins essential to the normal development of animals. But for a time it was not recognized that there are at least two fat-soluble vitamins in cod-liver oil. The investigations by which it was established that one of these, vitamin A, is concerned primarily with growth and the prevention of xerophthalmia, and that another, vitamin D, is concerned with the prevention of rickets, lie for the most part beyond the scope of our subject matter.

As early as 1922, Hume¹⁷ showed that rats on a vitamin A-deficient diet could not be protected from the effects of the lack of this vitamin by irradiation if the experiment was continued for a sufficient period. It followed that this vitamin is not produced in the animal as a result of photochemical processes. This was also the conclusion of Goldblatt and Soames¹⁸ from independent experiments. Sheets and Funk¹⁹ similarly found that on a diet deficient in fat-soluble vitamins (then called incorrectly vitamin A) a three- to five-minute daily irradiation by ultraviolet light prevented the appearance of rickets and, although the rate of growth of the animals was normal, xerophthalmia developed. Powers, Park and Simmonds²⁰ clearly recognized the existence of two separate factors or vitamins in cod-liver oil, the antixerophthalmic A and the antirachitic D.

It was next shown by Goldblatt and Soames²¹ that so long as the necessary vitamins are supplied in the diet light is not essential. Other experiments prior to the recognition of vitamins A and D as separate entities were by Eckstein²²

Steenbock and Nelson²³ found that such antirachitic agents as ultraviolet rays or cod-liver oil would restore the growth of rats maintained on a diet deficient in the fat-soluble vitamins but would not postpone the onset of xerophthalmia. They viewed these results as supporting the view that cod-liver oil contains two vitamins. It was also shown that non-irradiated rats receiving a diet deficient in the antirachitic factor showed normal growth when placed in the same cage with irradiated rats on the same diet. The same effect was obtained when the rats were placed in a jar on a galvanized iron wire screen contaminated slightly by other rats having been kept on them and then irradiated. It was necessary that the rats have access to the irradiated screen in order that they might ingest traces of excreta or skin secretions which had been irradiated. Irradiated air had no beneficial effects.²⁴

EFFECTIVE WAVE-LENGTH REGIONS

Once the effects of ultraviolet light in preventing the development of rickets had been established, the physical aspects of the process were studied to learn more precisely which wave-lengths are effective. Pappenheimer and Weinstock,²⁵ by interposing standard glass filters, found that wave-lengths as long as 3340Å had no protective action, the effective rays being in the neighborhood of 3130Å. Hess and Weinstock²⁶ thought the wave-length must not be longer than 3130Å and found the effectiveness of the 3020Å line very great. Mouriquand, Bernheim and

¹⁷ Hume, E. M., *Lancet*, **II**, 1318 (1922).

¹⁸ Goldblatt, H., and Soames, K. M., *Lancet*, **II**, 1321 (1922).

¹⁹ Sheets, O., and Funk, C., *Proc. Soc. Exptl. Biol. Med.*, **20**, 80 (1922); *Chem. Abs.*, **17**, 3528 (1923).

²⁰ Powers, G. F., Park, E. A., and Simmonds, N., *Proc. Soc. Exptl. Biol. Med.*, **20**, 81 (1922).

²¹ Goldblatt, H., and Soames, K. M., *Biochem. J.*, **17**, 294, 622 (1923).

²² Eckstein, A., *Arch. Kinderheilk.*, **73**, 1 (1923); Allenbach and Simon, R., *Rev. Hyg. Soc. Strasbourg*, **81**, 670 (1923); *Bull. Soc. Hyg. Aliment.*, **11**, 124 (1923); *Chem. Abs.*, **17**, 2306 (1923).

²³ Steenbock, H., and Nelson, M. T., *J. Biol. Chem.*, **56**, 355 (1923); see also *Ibid.*, **62**, 575 (1925) and Steenbock, H., Nelson, M. T., and Black, A., *Ibid.*, **62**, 275 (1924).

²⁴ For further discussion of the separate assay of vitamins A and D on rats see Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.*, **69**, 277 (1926) and Sherman, H. C., and Hessler, M. C., *J. Biol. Chem.*, **73**, 113 (1927).

Theobalt²⁷ observed that rats irradiated five minutes daily by a mercury arc with an interposed Wood's glass filter developed rickets, but that those receiving 90 minutes of irradiation under these conditions did not. Luce²⁸ found that a filter transmitting 5 per cent of the incident light at 8050A and cutting off completely at 2960A destroyed the effectiveness of irradiation, but that a screen transmitting 80 per cent at 3000A and letting through some rays to 2400A, and one transmitting 77 per cent at 3000A and cutting off between 2650 and 2450A, each transmitted the effective rays. Hess and Weinstock²⁹ believed that wave-lengths shorter than those available in sunlight had even greater potency. They noted during the winter months when the shorter wave-lengths do not reach the earth, and even the longer ones reach it with lowered intensity, that the effective wave-lengths available are reduced to a band only about 50A wide, between 3130 and 3080A. Maughan³⁰ found the wave-length 2968A four times as effective as 3020A.

Huldschinsky³¹ once proposed to term rays of wave-length longer than 3200A, ultraviolet A, those between 3200 and 2890A ultraviolet B (standing for biologically active), and those shorter than 2890A, ultraviolet C. This suggestion failed to find general favor.

Bunker and Harris³² advocated an attitude of caution in regard to the acceptance of the view that only a narrow band near 3000A is of importance.

AMOUNTS OF ENERGY REQUIRED

Recent studies indicate that the most effective wave-length for curing rickets in rats is 2804A.³³ To produce healing equivalent to that due to one international unit of vitamin D, the following energies (in thousands of ergs) were required at various wave-lengths: 2653A, 287; 2804A, 226; 2894A, 395; 2967A, 280; 3024A, 553; 3128A, 27,545. Prolonged irradiation, particularly by the shorter wave-lengths 2653, 2804 and 2894A has a destructive action. Stein and Lewis³⁴ found that at Denver, direct sunlight in June and July was effective for rats in exposures as short as 3.75 minutes daily. Curative effects are produced in either chickens or human infants by irradiation by even, in some cases, tungsten filament lamps in thin Correx D glass bulbs, according to Maughan and Dye,³⁵ and Gerstenberger and Horesh.³⁶ In the case of the children, continuous exposures were given for twelve hours to two lamps six feet apart housed in oxidized aluminum reflectors five and a half feet above the bed level. Hauch and Hanke³⁷ found that February sunlight at the street level in Chicago failed to protect rats on a rachitic diet and exposed behind commercial ultraviolet glasses. Under the same conditions, however, they were protected fully by March to April sunlight. Control rats behind ordinary glass were not protected.

²⁶ Pappenheimer, A. M., and Weinstock, M., *Proc. Exptl. Biol. Med.*, **20**, 14 (1922).

²⁷ Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **80**, 687 (1922).

²⁸ Mouriquand, G., Bernheim, M., and Theobalt, Mille., *Compt. rend.*, **182**, 1490 (1926).

²⁹ Luce, E. M., *J. Biol. Chem.*, **71**, 187 (1926).

³⁰ Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **89**, 1222 (1927).

³¹ Maughan, G. H., *Am. J. Physiol.*, **87**, 381 (1928).

³² Huldschinsky, K., *Klin. Wochschr.*, **5**, 1972 (1926).

³³ Bunker, J., and Harris, R., *Am. J. Public Health*, **20**, 1278 (1930).

³⁴ Knudson, A., and Benford, F., *J. Biol. Chem.*, **124**, 287 (1938).

³⁵ Stein, H. B., and Lewis, R. C., *Am. J. Diseases of Children*, **41**, 62 (1931).

³⁶ Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, **20**, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, **28**, 106 (1930).

³⁷ Gerstenberger, H. J., and Horesh, A. J., *J. Am. Med. Assoc.*, **96**, 766 (1931).

³⁸ Hauch, J. T., and Hanke, M. E., *Ind. Eng. Chem.*, **23**, 1398 (1931).

In New Orleans, Mayerson and Laurens³⁸ found the following to be the minimal daily times of irradiation necessary: February and March, 3 to 5 minutes for chicks and 5 to 6 minutes for rats. For either, the times were from April through October, 3 to 5 minutes, and from November through January, 5 to 6 minutes. The average daily amount of direct solar radiation of wave-length shorter than 3130A that will prevent rickets in rats is less than 0.001 calorie per sq. cm. from April to October, and between 0.001 and 0.002 calorie during the rest of the year. Of course, it is necessary to consider the number of sq. cm. exposed at such intensities since there is a minimal dose of vitamin D which must be produced in the total irradiated area for the protective action to become effective. For the prevention of leg weakness in chicks the amount of energy required was found to be about 0.00069 calorie per sq. cm. daily.

Children need have only a small portion of their bodies irradiated for successful results. Thus Catel³⁹ found it necessary to irradiate only the face or any area of 90 sq. cm.

There have been several other studies of the effectiveness of winter sunshine at various geographical locations. Tisdall and Brown,⁴⁰ working at Toronto, found that a marked increase in the antirachitic effect of sunshine occurs whenever the sun reaches an altitude of 35° or more. Geographically, rickets is uncommon or exists in but a mild form in those places where the minimal seasonal altitude of the sun is not below this angle, and severe rickets is chiefly encountered in those cities where the altitude is below that value for some months of the year. At Toronto, the antirachitic effect of the skyshine was about one-half to two-thirds as great as that of sunshine, by which is meant both the direct rays from the sun and the rays reflected from the sky and clouds. Even December skylight had a definite antirachitic effect. Fleming⁴¹ found that at Washington, D. C., the winter sunlight is antirachitic for rats after passing through Vitaglass. Under the same conditions, north skylight was also protective during the months of April, May, June and July. At Boston, Wyman⁴² found it possible to cure rickets in the winter months by exposures to sunlight through quartz windows or Corning glass windows, although the results were less favorable with Vitaglass. (See Chapter 10.) Favorable results were obtained also by means of Cel-O-Glass windows.⁴³ Jendrassik and Papp⁴⁴ found that at Budapest the sunlight was ineffective during December and January. Its activity then rose to a sharp and high peak at mid-June and declined again practically at the same rate.

A painstaking investigation of the energy required is that of Sonne and Rekling,⁴⁵ who employed a monochromator and determined by means of a thermopile the energy in gm. calories per sq. cm. incident at each of several wave-lengths on an area of the experimental animals of 8.1 sq. cms. In this way it was possible to eliminate the relative intensities of the various lines emitted by the source. The effect of the 3130A line was doubtful, although the incident energy amounted to $4.3 \times 0.708 \times 10^{-4}$ gm. cal. per sq. cm. per minute. At 3020 to 2970A with a somewhat lower intensity ($3 \times 0.708 \times 10^{-4}$ gm. cal. per sq. cm. per minute) there was a strong antirachitic action. This was also the case at 2650A, although the intensity was lower, $1.5 \times 0.708 \times 10^{-4}$ gm. cal. It was also

³⁸ Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, 102, 422 (1932).

³⁹ Catel, W., *Monatschr. Kinderheilk.*, 54, 426 (1932); *Chem. Abs.*, 27, 2184 (1933).

⁴⁰ Tisdall, F. F., and Brown, A., *Can. Med. Assoc. J.*, 20, 253 (1929); *Chem. Abs.*, 23, 3007 (1929); *Am. J. Diseases of Children*, 34, 721, 737, 742 (1927); 36, 734 (1928); *J. Am. Med. Assoc.*, 92, 860 (1929); 94, 854 (1930).

⁴¹ Fleming, W. D., *Military Surgeon*, 62, 592 (1928); 63, 658 (1928).

⁴² Wyman, E. T., *Boston Med. & Surg. J.*, 197, 376 (1927).

⁴³ Wyman, E. T., Drinker, P., and Mackenzie, K. H., *Am. J. Diseases of Children*, 39, 969 (1930).

⁴⁴ Jendrassik, A., and Papp, S., *Biochem. Z.*, 268, 364 (1934). In these experiments ergosterol rather than patients or experimental animals was irradiated.

⁴⁵ Sonne, C., and Rekling, E., *Strahlentherapie*, 25, 552 (1927); cited by Laurens, H., "The Physiological Effects of Radiant Energy," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1933.

strong at 2530A where the intensity was slightly greater, $1.6 \times 0.708 \times 10^{-4}$ gm. cal. On the other hand, at 2480 and at 2390A where the energies were respectively 0.7 and $0.55 \times 0.708 \times 10^{-4}$ gm. cal. per sq. cm. per minute, there was but slight action. No protection was afforded by the wave-lengths 2270 to 2200A, with $0.4 \times 0.708 \times 10^{-4}$ gm. cal. per sq. cm. per minute.

The opinions of workers who have studied the influence of the pigment of the skin on the curative effects of sunlight differ somewhat. Schultzer and Sonne and Hess, and Unger and Pappenheimer believe that pigmentation in rats somewhat lessens the effects of irradiation. In children, however, Kramer, Casparis and Howland, as well as Levinsohn,⁴⁶ conclude that the skin pigment of the Negro child does not interfere with the action of ultraviolet rays.

Gerstenberger and Hartman⁴⁷ found that quartz lamp exposures weekly with doses of one erythema unit for negro infants, and less for white infants, applied to both front and back, caused healing in practically the same time as did heavier doses. Gerstenberger and Russell⁴⁸ obtained similar results with the General Electric Sunlamp S-1. Using a quartz lamp at 80 cm., Vollmer found a weekly dose of from four to five minutes each to the chest and back to be the minimal effective dose. Cures were effected after the application of about 100 minutes of treatment.

EFFECTS ON MINERAL METABOLISM.

Ultraviolet irradiation cannot overcome mineral deficiencies of the diet. Its function is to supply the vitamin D necessary to control the proper utilization of the calcium and phosphorus in the diet. Theiler⁴⁹ emphasized the fact that when the phosphorus of the diet of cattle is deficient rickets will develop in the presence of abundant solar radiations. Many papers have been devoted to the effects of irradiation upon the blood phosphorus and calcium levels during the cure of rickets. In contrast to the negative results discussed in the preceding chapter in regard to the influence of irradiation upon these values in the normal individual, there is general agreement that if the mineral contents of the diet are suitable, the low values which characterize rickets are readily restored to normal by irradiation or by the administration of vitamin D.

Kramer, Casparis and Howland⁵⁰ found values for the inorganic phosphorus in the serum of the blood of rachitic infants to vary from 2.7 to 3.2 mgm. per cent. Under quartz lamp treatment, this increased gradually to a maximum of 6 mgm. per cent, the normal value. Hess and Lundagen⁵¹ observed a seasonal variation in the level of the inorganic phosphates of the blood corresponding to and determined by the seasonal variations in the ultraviolet energy of the available solar spectrum.

By 1923, it was⁵² reported that the mean serum calcium content of normal infants from two months to ten years of age varies between 10 and 12 mgm. per 100 cc. In twenty rachitic infants, it ranged from 7.9 to 10.4 mgm. with an average of about 9.2. Two children of three and eight years with irreducible

⁴⁶ Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, 24, 20 (1927); Levinsohn, S. A., *Ibid.*, 34, 955 (1927).

⁴⁷ Gerstenberger H. J., and Hartman, J. I., *J. Am. Med. Assoc.*, 92, 367 (1929).

⁴⁸ Gerstenberger, H. J., and Russell, G. R., *J. Am. Med. Assoc.*, 94, 1049 (1930); Vollmer, H., *Klin. Wochschr.*, 9, 2300 (1930).

⁴⁹ Theiler, A., *Veterinary J.*, 90, 159 (1934); *Chem. Abs.*, 28, 5503 (1934).

⁵⁰ Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, 24, 20 (1922).

⁵¹ Hess, A. F., and Lundagen, M. A., *J. Am. Med. Assoc.*, 79, 2210 (1922).

⁵² Lesné, E., deGennes, L., and Guillaumin, *Compt. rend.*, 177, 291 (1923); *Chem. Abs.*, 17, 3540 (1923); see also Kramer, B., and Boone, F. H., *Proc. Soc. Biol. Exptl. Med.*, 20, 87 (1922).

rachitic deformations had normal or slightly greater amounts of calcium, 11.8 and 11.4 mg. respectively. The calcium content of the serum is not modified by the injection of calcium chloride, but is altered by ultraviolet rays. After eight daily irradiations of thirty minutes each at 1.2 meters from a 1200 c.p. carbon arc given ten infants the serum calcium was decidedly increased in seven and after 24 irradiations it was well up to the normal value in eight of the children. The two infants which failed to show an increase in the calcium had dark skins. Orr, Holt, Wilkins and Boone⁵³ also showed that infants with active rickets are unable to retain calcium and phosphorus even though these elements are present in adequate amounts in the diet and that ultraviolet rays cause these elements to be retained. They observed that after irradiation increased amounts of these elements are found in the urine, indicative of an increased absorption of these essential minerals from the intestine. They argued that defective intestinal absorption in rickets is the cause of the low serum calcium and phosphorus, and is the ultimate cause of the defective calcification of the bones. That calcification at the junction of the bones and cartilage could be promoted by irradiation also was demonstrated radiographically by Vignard, Mouriquand, Chassard and Bernheim.⁵⁴

Clark⁵⁵ reported that the diffusible calcium of the serum, measured by dialysis in collodion sacks against physiological salt solution, may be increased by subjecting it to quartz mercury arc irradiations. The diffusible calcium in rabbit serum rose from 38 to 58% and in dog serum from 44 to 53%.

Hart, Steenbock and Elvehjem⁵⁶ induced experimentally negative calcium balances in mature lactating goats. Daily mercury arc irradiation changed these to positive and also appreciably increased the blood phosphorus. This was confirmed by Orr, Henderson and Magee,⁵⁷ who believed the results might be accounted for by a decreased elimination of calcium in the feces, the urinary excretion remaining practically constant. These results favored the view that irradiation induces an increased absorption of calcium from the intestines.

Schultzer⁵⁸ defines the Ca retention coefficient as the number of mg. retained per g. increase in body weight of rats during growth. The coefficient was 4.7 to 5.2 in young rats on a rachitic diet and with evident rickets. After irradiation, it was raised to 10. For phosphorus the values were 8.1 to 9.5 before and 15.7 after the cure of the rickets. Similar results also could be brought about by giving the rats cod-liver oil or, if the diet was deficient in phosphorus, by giving phosphates. A number of rachitic rats showed an average of 11.9 mgm. of calcium and 5.6 mgm. of phosphorus per 100 cc. of serum.⁵⁹

In four ultraviolet-treated rats the serum calcium rose to 15.2 and the phosphorus to 8.6 mgm. per 100 cc. Normal rats on an ordinary diet failed to show this rise during irradiation. Burton⁶⁰ found in boys who had received some ultraviolet irradiation while on a diet high in calcium and phosphorus a high retention of these elements.

After daily exposures of gravid rats to sunlight, the lime of the fetuses increased 21.2

⁵³ Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, 26, 362 (1923).

⁵⁴ Vignard, Mouriquand, Chassard, and Bernheim, *Lyon Medicale*, 132, 1021 (1923); *Chem. Abs.*, 18, 2382 (1924); Lesné, E., de Gennes, L., and Guillaumin, C., *Compt. rend.*, 177, 291 (1923); *Chem. Abs.*, 17, 3540 (1923); Howland, J., and Kramer, B., *Am. J. Diseases Children*, 22, 105 (1921); *Chem. Abs.*, 17, 413 (1923).

⁵⁵ Clark, J., *Am. J. Hyg.*, 3, 481 (1923); *Chem. Abs.*, 18, 2366 (1924).

⁵⁶ Hart, E. B., H. Steenbock and C. A. Elvehjem, *J. Biol. Chem.*, 62, 117 (1924).

⁵⁷ Orr, J. B., Henderson, J. M., and Magee, H. E., *Biochem. J.*, 19, 569 (1925).

⁵⁸ Schultzer, P., *Compt. rend. soc. biol.*, 93, 1005 (1925); *Chem. Abs.*, 20, 1655 (1926); *Biochem. Z.*, 188, 409, 427 (1927); Mitchell, H. F., and Johnson, F., *Am. J. Physiol.*, 72, 143 (1925); Koch, E. M., and Cahan, M. H., *Am. J. Diseases of Children*, 34, 187 (1927).

⁵⁹ Schultzer, P., *Compt. rend. soc. biol.*, 93, 1008 (1925); *Chem. Abs.*, 20, 1655 (1926).

⁶⁰ Burton, H. B., *J. Biol. Chem.*, 85, 405 (1930).

per cent and the phosphate 19.2 per cent over that of the fetuses of non-irradiated rats. The phosphatase content, however, was not affected, according to Foa.⁶¹

Subsequent studies of the calcium and phosphorus in the blood serum in rickets have indicated that the disease may appear with either low phosphorus or low calcium or with both low in the serum. But if one is low and the other high there may be no rickets.⁶² Kramer, Shear and Siegel⁶³ found the product of the calcium and phosphorus concentrations to be always thirty or less during rickets or during the cessation of calcification. When the product rises above forty, calcification may ensue no matter whether the healing is induced by cod-liver oil, phosphates, or artificially prepared vitamin D. There are, however, many recorded exceptions to this rule. Dietary ratios of calcium and phosphorus are important.⁶⁴ Many other papers deal with this topic, but are beyond the scope of this discussion.

At one time it was believed that an alteration of the pH of the substances in the intestinal tract was, in part at least, responsible for the failure of the proper absorption of calcium from the gut in rickets. Jephcott and Bacharach⁶⁵ stated that the alkalinity of the feces of animals on rachitic diets could be brought to the acid side of neutrality by irradiations or by administering cod-liver oil. It was assumed that determinations of the change in pH induced by various preparations containing vitamin D might be made the basis of an assay method for this vitamin. Wokes and Willimott⁶⁶ found that the method could not be applied to infants although they believed it gave satisfactory results in rats. Subsequent investigations, however, have shown the method unreliable.

The irradiation of nursing mothers whose breast milk had been failing was of general benefit in all of 53 cases in which the treatment was continued for some time, and was of aid in improving or retaining the milk supply in all but eleven of the cases.⁶⁷ Hess, Weinstock and Sherman⁶⁸ found that exposing a woman to the rays of a mercury-vapor quartz lamp every other day for a month produced antirachitic properties in her milk when fed to rats. During the control period the milk had no curative action. In similar experiments, Hirsch-Kauffmann and Wiener⁶⁹ found the quantity of the milk of irradiated mothers to be increased, although its chemical composition was unaltered except for a definite increase in vitamins C and D.

In children with various orthopedic disorders, exposure to all the sunshine available from May to August was not found to produce any symptoms characteristic of an overdose of vitamin D.⁷⁰

APPLICATIONS IN ANIMAL HUSBANDRY

During the early development of irradiation therapy, attention was also devoted to the effects of ultraviolet light on farm animals. Hart, Steenbock and Jones⁷¹ concluded that sunlight is a factor of economic importance in the production of pork in northern latitudes, and Maynard, Goldberg and Miller in New York⁷²

⁶¹ Foa, P., *Boll. soc. ital. biol. sper.*, 11, 845 (1936); *Chem. Abs.*, 31, 2622 (1937).

⁶² See Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929. Note also Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, 26, 362 (1923); Hess, A. F., Weinstock, M., Rivkin, H., and Gross, J., *J. Biol. Chem.*, 87, 37 (1930); Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, 94, 1885 (1930).

⁶³ Kramer, B., Shear, M. J., and Siegel, J., *J. Biol. Chem.*, 91, 271, 723 (1931).

⁶⁴ See also Shohl, A. T., and Bennett, H. B., *J. Biol. Chem.*, 76, 633 (1928); Reed, C. I., Struck, H. C., and Steck, I. E., "Vitamin D" Chicago, Univ. of Chicago Press, 1939.

⁶⁵ Jephcott, H., and Bacharach, A. L., *Biochem. J.*, 20, 1351 (1926).

⁶⁶ Wokes, F., and Willimott, S. G., *Pharm. J.*, 118, 752, 793 (1927).

⁶⁷ Chisholm, C., and McKillop, M., *Lancet*, II, 227 (1927); *Chem. Abs.*, 22, 2384 (1928).

⁶⁸ Hess, A. F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, 23, 636 (1926).

⁶⁹ Hirsch-Kauffmann, H., and Wiener, C., *Klin. Wochschr.*, 8, 984 (1929); *Chem. Abs.*, 23, 4970 (1929).

⁷⁰ Dodds, E. C., Robertson, J. D., and Roche, H. J., *Arch. Diseases of Childhood*, 9, 91 (1934); *Chem. Abs.*, 28, 4459 (1934).

⁷¹ Hart, E. B., Steenbock, H., and Jones, J. H., *J. Biol. Chem.*, 61, 775 (1924).

⁷² Maynard, L. A., Goldberg, S. A., and Miller, R. C., *J. Biol. Chem.*, 65, 643 (1925).

found that sunlight improves the assimilation of calcium from a deficient diet and prevents the development of leg weakness in pigs. In a general discussion, Price⁷³ stated that besides an adequate amount of calcium and phosphorus in the diet of pigs it is essential for their health and growth that there also must be present either the antirachitic vitamin or exposure to sunlight. Henderson⁷⁴ found that the calcium and phosphorus retention of pigs receiving a poorly balanced diet, with $P_2O_5:Ca:Mg$ as 3:1:1, was definitely increased by an irradiation of one hour per day for 24 days. No corresponding increase in body weight occurred, however.

It was believed by Bohstedt, Insko and Fargo⁷⁵ that for the health of the suckling pig dependence must be placed upon the antirachitic properties of the feed of the sow rather than upon the use of ultraviolet light, helpful as this may be. According to Isaachsen,⁷⁶ irradiation of sows in the last six weeks of gestation and of sows with litters did not improve the growth or condition of the pigs. He believed that pigs are more likely to suffer from disordered mineral metabolism as a result of a deficiency of minerals in the food or from an incorrect calcium-to-phosphorus ratio than from a lack of fat-soluble vitamins. Sinclair⁷⁷ found exposure to either sunlight or artificial sources, as well as cod-liver oil feeding, to promote growth in the pig, the response being inversely proportional to the calcium content of the basal ration. The addition of calcium to the ration aided greatly in the prevention of leg stiffness, a condition resembling rickets. Irradiation increased the level of the blood calcium.

Calves also require vitamin D. Calves fed on rations deficient in it show declining growth rates at the twelfth to the fifteenth week; and after the twenty-fifth week little growth occurs.⁷⁸ A decline in the level of inorganic phosphorus in the blood serum precedes the onset of stiffness. The percentage of total ash in the dry, fat-free bones is reduced from the normal of 60 to 63 per cent to 45 to over 50 per cent in the rachitic bones. The breaking strength of the bones also is lowered. Ultraviolet irradiation, sunlight or the feeding of liberal amounts of sun-cured hay protects the calves from the vitamin D deficiency.

Bechdel, Landsburg and Hill⁷⁹ also noted the abnormal bone development, swollen joints, and slight paralysis of the rear quarters and bowed back of vitamin D-deficient calves. Although cod-liver oil promoted growth and thriftiness slightly better than did ultraviolet light treatment, the latter produced a slightly superior grade of bone. Direct sunlight is not required if the ration contains sufficient vitamin D.⁸⁰

The vitamin D requirement of dogs has been studied by Morgan.⁸¹ Symptoms of rickets have been developed in a newly weaned cat fed 24 days on the Steenbock diet deficient in calcium and vitamin D.⁸²

⁷³ Price, W. A., *Ind. Eng. Chem.*, **18**, 679 (1926).

⁷⁴ Henderson, J. M., *Biochem. J.*, **19**, 52 (1925); *Scottish J. Agr.*, **9**, 33 (1926); *Chem. Abs.*, **20**, 2523 (1926). See also Orr, J. B., Henderson, J. M., and Crichton, J. A., *Trans. Highland Agr. Soc. Scotland*, **38**, 88 (1926).

⁷⁵ Bohstedt, G., Insko, W. M., Jr., and Fargo, J. M., *Proc. Am. Soc. Animal Production*, **89** (1929), *Chem. Abs.*, **25**, 3695 (1931); see also Thalman, R. R., and Loeffel, W. J., *Proc. Am. Soc. Animal Production*, **83** (1928); *Chem. Abs.*, **25**, 3695 (1931).

⁷⁶ Isaachsen, H., *J. Agr. Sci.*, **22**, 460 (1932); *Chem. Abs.*, **27**, 1916 (1933).

⁷⁷ Sinclair, R. D., *Sci. Agr.*, **13**, 489 (1933); *Chem. Abs.*, **27**, 5787 (1933); Horn, V., *Biedermann's Zentralbl. B. Tierernähr.*, **6**, 203, 208 (1934); *Chem. Abs.*, **28**, 5855 (1934).

⁷⁸ Rupel, I. W., Bohstedt, G., and Hart, E. B., *Wisconsin Agr. Exp. Sta. Research Bull.*, **115**, 40 pp. (1933); *Chem. Abs.*, **28**, 507 (1934).

⁷⁹ Bechdel, S. I., Landsburg, K. G., and Hill, O. J., *Pennsylvania Agr. Exp. Sta. Tech. Bull.*, **291**, 2 (1933); *Chem. Abs.*, **28**, 3028 (1934).

⁸⁰ Olson, T. M., *S. Dakota Agr. Exp. Sta., Bull.* **319**, 2 (1938); *Chem. Abs.*, **32**, 7970 (1938).

⁸¹ Morgan, A. F., *North American Veterinarian*, **15**, No. 8, 24 (1934); *Chem. Abs.*, **29**, 201 (1935).

⁸² Moody, C. A., *J. Home Econ.*, **28**, 696 (1936); *Chem. Abs.*, **31**, 436 (1937).

Irradiation and Poultry Culture. Because of the modern intensive methods of poultry culture, vitamin D deficiencies are quite common. Their remedy is a matter of considerable economic importance. Murray, Little and Bovie⁸³ found chicks exposed for only a few minutes each day to the rays of the mercury arc showed a more rapid formation of bone than did chicks exposed for many hours daily to direct sunlight.

Hughes, Titus and Moore⁸⁴ found that chicks fed on eggs from hens which were receiving direct sunlight developed normally, as shown by their general appearance and by the analysis of their blood and bones. Those fed on eggs from hens which received sunlight filtered through glass and supplemented by thirty minutes per day from a mercury arc developed some rickets. They were, however, in a better condition than those receiving eggs from hens which received no ultraviolet light other than that which came through a glass window. They believed thirty minutes of ultraviolet irradiation daily insufficient to enable hens to store sufficient antirachitic vitamin in their eggs to prevent entirely the development of rickets in chickens fed rations containing these eggs. Eggs of low antirachitic vitamin content do not have as high a hatchability as those with high vitamin content.⁸⁵

Goodale⁸⁶ demonstrated that the amount of exposure to sunlight or ultraviolet light necessary for normal growth is but very small in the chick. Irradiations of one and ten minutes twice weekly at three feet from a mercury-vapor arc gave normal growth.⁸⁷

DeVancy, Munsell and Titus⁸⁸ found that daily fifteen-minute irradiations with a carbon arc had approximately the same effect on vitamin D storage by hens as the addition of 1 per cent of cod-liver oil to the diet.

Hou⁸⁹ found rachitic chicks with intact preen glands to be cured when either the body, feet or head was irradiated. The degree of healing was greatest with the irradiation of the feet and least with the head. Rachitic chicks with the preen glands removed were not cured when the head was irradiated, but irradiation of the feet produced good healing. The substance which is activated when the feet are irradiated is apparently neither the preen gland material nor the circulating blood. Russell and Howard⁹⁰ delayed the onset of leg weakness in young chicks for about a week by an exposure to one day of winter sunlight through an ultraviolet transmitting material. There was also an indication of an effect on bone formation. A three-day exposure delayed the appearance of leg weakness about two and a half to three weeks and had a more enduring effect on bone formation.

Either cod-liver oil or ultraviolet irradiation of laying hens kept without access to direct sunlight or green feed increased the egg production, the thick-

⁸³ Murray, J. M., Little, C. C., and Bovie, W. T., *Maine Agr. Exp. Sta. Bull.* 320, 141 (1924); *Chem. Abs.*, 19, 3105 (1925).

⁸⁴ Hughes, J. S., Titus, R. W., and Moore, J. M., *Science*, 62, 492 (1925); *Chem. Abs.*, 20, 936 (1926); Hughes, J. S., Payne, L. F., Titus, R. W., and Moore, J. M., *J. Biol. Chem.*, 66, 595 (1925).

⁸⁵ For the amounts of the vitamin required for the production of hatchable eggs, see Bethke, R. M., and Kennard, D. C., *Proc. Fourth World's Poultry Congress*, 342 (1930); *Chem. Abs.*, 25, 4027 (1931). It has been suggested that sunlight may increase the hatchability of eggs by some mechanism other than vitamin D. Byerly, D. C., Titus, H. W., Ellis, N. R., and Nestler, R. B., *Poultry Sci.*, 16, 322 (1937); *Chem. Abs.*, 31, 8625 (1937).

⁸⁶ Goodale, H. D., *Am. J. Physiol.*, 79, 44 (1926).

⁸⁷ Cf. also Price, W. A., *Science*, 63, 1636 (1926); Russell, W. C., Massengale, O. N., and Howard, C. H., *J. Biol. Chem.*, 80, 155 (1928); Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, 20, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, 26, 106 (1930).

⁸⁸ DeVancy, G. M., Munsell, H. E., and Titus, H. W., *Poultry Sci.*, 12, 215 (1933); *Chem. Abs.*, 27, 5380 (1933).

⁸⁹ Hou, H.-C., *Chinese J. Physiol.*, 5, 11 (1931); *Chem. Abs.*, 25, 3037 (1931); see also Murphy, E. F., *J. Agr. Research*, 53, 67 (1936); *Chem. Abs.*, 30, 8319 (1936).

⁹⁰ Russell, W. C., and Howard, C. H., *J. Biol. Chem.*, 91, 493 (1931).

ness of the egg shells and the general condition of the birds, according to Hendricks, Lee and Godfrey.⁹¹ Each of these methods of supplementing the vitamin D also tended to increase the egg weight and the hatchability of the eggs. Cod-liver oil was superior to fifteen minutes of daily irradiation under the conditions employed. Dove⁹² believed the chick superior to the rat for vitamin D research because it is more sensitive than the latter to a deficiency of that vitamin. Payne and Hughes⁹³ found direct sunshine somewhat more effective than ultraviolet irradiations from artificial sources in increasing the calcium content of the hen blood, of eggs and of newly hatched chicks. Maughan and Maughan⁹⁴ noted that ultraviolet irradiation of hens increases the vitamin D content of the egg yolk.⁹⁵

Further studies on the vitamin D requirement of the chick have played an important part in the development of our knowledge of the chemistry of vitamin D and will be considered in the following chapter after the chemical changes underlying the formation of this substance have been discussed.

THE IRRADIATION OF FOODSTUFFS

During the years 1924 and 1925 it was discovered that, on analogy with the formation of antirachitic substances in the skin of irradiated animals, antirachitic potency is imparted to foodstuffs when these are submitted to the action of ultraviolet rays. Hume and Smith⁹⁶ were very near this important discovery when they reported that rats fed on a diet deficient in fat-soluble vitamins and kept in glass jars which had been exposed to quartz lamps for ten minutes every second day showed a prolongation of growth at a normal rate longer than that of controls kept in jars not so irradiated. Their work was conducted to determine whether the irradiation of the air played a part in the mechanism of the antirachitic resistance of irradiated animals. They showed definitely that ozone was not the effective agent, but overlooked the real cause of the beneficial effect they observed. Webster and Hill⁹⁷ showed that irradiated air could not have produced the beneficial results, and Hume and Smith later reported⁹⁸ that their results could be obtained only when the glass jars which were irradiated contained sawdust. When this was replaced by a piece of pine board, partial growth only resulted.⁹⁹ They had, however, missed their opportunity, for in the meantime Hess and Weinstock, as well as Steenbock and Black, had independently shown that certain foodstuffs can be rendered antirachitically active by irradiation.

On June 7, 1924, Hess reported the results of experiments conducted with Weinstock to the American Pediatrics Society¹⁰⁰ which indicated that vegetable

⁹¹ Hendricks, W. A., Lee, A. R., Godfrey, A. B., *J. Agr. Research*, **43**, 517 (1931); *Chem. Abs.*, **26**, 1324 (1932).

⁹² Dove, W. F., *Maine Agr. Exp. Sta. Bull.*, **360**, 172 (1931); *Chem. Abs.*, **27**, 1918 (1933).

⁹³ Payne, L. F., and Hughes, J. S., *Kansas Agr. Sta. Tech. Bull.*, **34**, 5 (1933); *Chem. Abs.*, **27**, 4277 (1933).

⁹⁴ Maughan, G. H., and Maughan, E., *Brit. J. Phys. Med.*, **7**, 137 (1932); *Chem. Abs.*, **27**, 5377 (1933).

⁹⁵ For calcium and phosphorus determinations in chicken blood, see Elvehjem, C. A. and Kline, B. E., *J. Biol. Chem.*, **103**, 733 (1933), and Higgins, G. M., Sheard, C., and Wilder, R. M., *Anat. Record*, **58**, 205 (1934).

⁹⁶ Hume, E. M., and Smith, H. H., *Biochem. J.*, **17**, 364 (1923).

⁹⁷ Webster, T. A., and Hill, L., *Proc. Physiol. Soc., J. Physiol.*, **57**, LXXVIII (1923); *Chem. Abs.*, **18**, 278 (1924).

⁹⁸ Hume, E. M., and Smith, H. H., *Biochem. J.*, **18**, 1334 (1924).

⁹⁹ It was later shown by Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 1340 (1926) that a chloroform extract of irradiated sawdust has antirachitic activity.

¹⁰⁰ Hess, A. F., and Weinstock, M., *Abstracted in Am. J. Diseases of Children*, **28**, 256 (1924); **28**, 517 (1924). Also reported at a meeting of the New York Section, *American Chemical Society*, Jan. 9, 1925.

oils can be endowed with antirachitic properties on irradiation. Like Smith and Hume, they had started by attempting to activate air by ultraviolet light but obtained completely negative results. Their first favorable results were obtained when they irradiated cottonseed oil.¹⁰¹

Steenbock and Black¹⁰² in a paper received for publication April 18, 1924, described an experiment in which a ration of hog millet 84, purified casein, 12, and salt, was irradiated for ten minutes at a distance of 23 inches from a Cooper-Hewitt quartz mercury-vapor lamp with a three-fourths inch arc operated at 120 volts. When fed, this ration produced a pronounced stimulation of the growth of rats. They also succeeded in imparting growth-promoting and bone-calcifying properties to olive oil and lard by this method. The activation took place when the ration was irradiated in an open dish or in a stoppered Pyrex or quartz flask filled with air or carbon dioxide, but it did not occur when the ration was irradiated in a brown glass bottle. The ash content of the bones of the rats receiving the irradiated ration was increased in percentage over that of rats receiving the same ration before irradiation. It was found also that the irradiation of fats, otherwise inactive in curing rickets, caused them to become active. Rations which ordinarily produced a wide rachitic metaphysis in the shaft bones of rats became antirachitic and promptly effected a rapid and complete healing of the lesion. Hess, in his complete paper, showed that although cottonseed and linseed oils could be activated by irradiation, this was not possible in the case of mineral oil, and also that ozonized water and hydrogen peroxide afforded no protection to rats on a deficient diet. Steenbock and Daniels¹⁰³ successfully produced antirachitic properties in a wide variety of foods, which included wheat, rolled oats, corn, hominy, meats, milk, egg-yolk and the vegetable oils. They suggested that it is the sterols in the foods which are altered during the irradiation process. Spinach was rendered antirachitic by Chick and Roscoe¹⁰⁴ and cabbage by Mellanby and Killick.¹⁰⁵ That the irradiation of cod-liver oil did not increase its antirachitic potency was demonstrated by Daniels and Brooks¹⁰⁶ and by Wyman, Holmes, Smith, Stockbarger and Pigott.¹⁰⁷

Hume, Smith and Smedley-Maclean¹⁰⁸ succeeded in inducing antirachitic activity in yeast fat by irradiation and Daniels and Pyle and Brooks¹⁰⁹ showed that the use of milk irradiated a half hour at a distance of two feet from a mercury arc rendered it capable of bringing about prompt improvement in young rats. Gates and Grant¹¹⁰ found that in normal rabbits the feeding of cod-liver oil or irradiated products did not produce changes in the relative

¹⁰¹ Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **62**, 301 (1924). Goldblatt, H., and Soames, K. M., *Biochem. J.*, **17**, 446 (1923), had found that the livers of irradiated animals restored the growth of animals which had been inhibited by feeding certain diets.

¹⁰² Steenbock, H., and Black, A., *J. Biol. Chem.*, **61**, 408 (1924); see also *Science*, **60**, 224 (1924); *J. Biol. Chem.*, **62**, 209 (1924).

¹⁰³ Steenbock, H., and Daniels, A. L., *J. Am. Med. Assoc.*, **84**, 1093 (1925).

¹⁰⁴ Chick, H., and Roscoe, M. H., *Biochem. J.*, **20**, 137 (1926).

¹⁰⁵ Mellanby, M., and Killick, E. M., *Proc. Physiol. Soc.*, **61**, xxiii (1926); *Chem. Abs.*, **20**, 3488 (1926). See also Drummond, J. C., Rosenheim, O., and Coward, K. H., *J. Soc. Chem. Ind.*, **44**, 135T (1925). For a clinical investigation of the curative value of irradiated food, see Mackay, H. M. M., and Shaw, H. F., *Lancet*, **I**, 82 (1926).

¹⁰⁶ Daniels, A. L., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.*, **24**, 971 (1927).

¹⁰⁷ Wyman, E. T., Holmes, A. D., Smith, L. W., Stockbarger, D. C., and Pigott, M. G., *Boston Med. & Surg. J.*, **195**, 525 (1926); *Am. J. Diseases Children*, **34**, 753 (1927). See also Haffner, F., and Pulewka, P., *Klin. Wochschr.*, **5**, 2113 (1926).

¹⁰⁸ Hume, E. M., Smith, H. H., and Smedley-Maclean, I., *Biochem. J.*, **22**, 27 (1928).

¹⁰⁹ Daniels, A. L., Pyle, S. I., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 821 (1926); *Chem. Abs.*, **21**, 1831 (1927).

¹¹⁰ Gates, F. L., and Grant, J. H. B., *Proc. Soc. Exptl. Biol. Med.*, **24**, 59 (1926).

weights of endocrine organs such as the external parathyroid and the hypophysis, although these organs are hypertrophied in rabbits after repeated exposure to the quartz mercury arc. It was shown by Goldblatt and Moritz¹¹¹ that irradiation does not increase the quantity of vitamin A in fats but forms only the antirachitic D.

Among the earlier suggestions regarding the mechanism by which irradiation may function was one which has been repeatedly discussed, but is no longer considered significant. Kugelmass and McQuarrie suggested that irradiation so alters the substances of foods as to make them capable during subsequent slow oxidation of emitting ultraviolet rays which affect a photographic plate.¹¹² As they themselves subsequently pointed out, many substances exhibit the property of affecting a photographic plate, the Russell effect; it bears little or no relation to the production of antirachitic activity and it is unnecessary to consider here the large number of papers by other workers who sought to explain the effect of irradiation upon foodstuffs in terms of this phenomenon.

For some time it was believed that the origin of the vitamin in the livers of fish could be attributed to their ingestion of other smaller fish which had in turn ingested diatoms in which the vitamin had been produced photochemically. There is, however, considerable evidence against this. Leigh-Clare was unable to detect the vitamin in the marine diatom *Nitzschia closterium*, and others¹¹³ were unable to demonstrate it in phyto- and zoö-plankton from the ocean.¹¹⁴ Bills¹¹⁵ found the capelin, the chief food of the Newfoundland cod, a poor source. The enormous differences in the potencies of the liver oils from various species of fish suggest species differences in the ability to synthesize the vitamin and not merely in its storage. Attempts to produce more vitamin D in fish livers by irradiation of the fish have been unsuccessful.

Sunflower oil can be activated by irradiation by sunlight or artificial ultraviolet light.¹¹⁶ The same is true of peanut oil.¹¹⁷ The irradiated mycelium of *Aspergillus oryzae*, added to the diet of chicks to the extent of 0.05 per cent, makes them superior in health, appetite and growth to the controls.¹¹⁸ Sun-dried alfalfa contains small amounts of vitamin D.¹¹⁹ Clover hay made with exposure to sunlight showed considerable calcifying power, but clover hay made in the dark was inactive. If excessively weathered, it is reduced in activity as compared with hay less exposed to dew and rain, but it may be improved by subsequent mercury-arc irradiation.¹²⁰

The potency of sun-cured hays is, however, too feeble to prevent the development of rickets in growing chicks fed ether extracts of the hays equivalent to a high concentration of the hay in the ration.¹²¹ From 7 to 10 gms. of dry corn silage per kg. of feed cures and prevents rickets in yearling calves and supplies sufficient vitamin D for normal growth and reproduction in dairy cows.¹²²

Völtz and Kirsch believed that grass germinated in darkness contains some of the antirachitic vitamin.¹²³

¹¹¹ Goldblatt, H., and Moritz, A. A., *J. Biol. Chem.* 71, 127 (1926).

¹¹² Kugelmass, I. N., and McQuarrie, I., *Science*, 60, 272 (1924); 62, 87 (1925); Drummond, J. C., and Coward, K. H., *J. Soc. Chem. Ind.*, 44, 255 (1925).

¹¹³ Leigh-Clare, J. L., *Biochem. J.*, 21, 368 (1927); Drummond, J. C., and Gunther, E. R., *Nature*, 126, 398 (1930).

¹¹⁴ Belloc, G., Fabre, R., and Simonnet, H., *Compt. rend.*, 191, 160 (1930).

¹¹⁵ Bills, C. E., *J. Biol. Chem.*, 72, 751 (1927).

¹¹⁶ Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U.S.S.R.*, 1, 207 (1936); *Chem. Abs.*, 31, 1854 (1937).

¹¹⁷ Rondoni, P., *Sperimentale*, 80, 443 (1926); *Chem. Abs.*, 21, 761 (1927).

¹¹⁸ Yokoyama, K., and Takata, R., *J. Agr. Chem. Soc. Japan*, 12, 909 (1936); *Chem. Abs.*, 31, 1468 (1937).

¹¹⁹ Scheunert, A., and Schieblich, M., *Biedermann's Zentr. B. Tierernährung*, 6, 112 (1934); *Chem. Abs.*, 28, 5102 (1934).

¹²⁰ Steenbock, H., Hart, E. B., Elvehjem, C. A., and Kletzien, S., *J. Biol. Chem.*, 66, 425 (1925).

¹²¹ See also Bechdel, S. I., Landaburg, K. G., and Hill, O. J., *Pa. Agr. Exp. Sta. Tech. Bull.* 291, 2 (1933); *Chem. Abs.*, 28, 2038 (1934).

¹²² Bechtel, H. E., Huffman, C. F., Duncan, C. W., and Hoppert, C. A., *J. Dairy Sci.*, 19, 359 (1936); *Chem. Abs.*, 30, 5617 (1936).

¹²³ Völtz, W., and Kirsch, W., *Biochem. Z.*, 186, 255 (1927).

Chapter 39

The Photochemistry of the Formation of Vitamin D

EARLY OBSERVATIONS REGARDING THE PRECURSOR

Following the discovery of the ability of irradiation to render foodstuffs antirachitically active, there began an active search to determine which components of these materials are effectively altered during the irradiation. Such components as chlorophyll, hemoglobin, glycerol, starch, alkaloids and the phosphatides of egg-yolk were soon eliminated.¹ It was soon demonstrated that the vitamin is a component of only the unsaponifiable fraction of irradiated oils and that the chief components of the unsaponifiable portions of the oils, the sterols, have the property of being activated by irradiation.² This was shown in the case of the phytosterol prepared from cottonseed oil and of cholesterol isolated from brain tissue. Since it was known that the skin of animals contains much cholesterol, Hess suggested that when the animal is irradiated it is the cholesterol of the skin which is changed, or as it was then said, activated.^{2a}

Steenbock and Black³ were able to impart antirachitic activity to purified cholesterol by irradiation with either a mercury arc, a carbon arc or direct sunlight. They observed the significant fact that irradiation for prolonged periods destroyed the activity of natural cod-liver oil and also the activity artificially produced by shorter irradiations of vegetable oils, although in darkness the activity was maintained as long as ten months. They believed that old oils which had become acid could no longer be activated, although this was not held due to the acidity as such, since the addition of oleic acid to the oil did not interfere with the process of activation.

That the antirachitic properties of irradiated cholesterol, like those of cod-liver oil, can be destroyed by heating with butyronitrile was believed by Bills⁴ to support, although not to prove, the identity of the irradiation product of cholesterol with the vitamin of cod-liver oil. That the rays which render cholesterol active are those which cure the animal in irradiation therapy was shown by Hess and Weinstock.⁵ They also showed that the dihydroderivatives of cholesterol or of the phytosterol of wheat could not be made to acquire antirachitic activity by irradiation. This indicated unsaturation to be a necessary, but not a sufficient condition, determining the ability of a compound to function as a precursor of the vitamin.

¹ Hess, A. F., Weinstock, M., *J. Biol. Chem.*, **63**, 297 (1925); **62**, 301 (1924); Drummond, J. C., Coward, K. H., and Rosenheim, O., *J. Soc. Chem. Ind.*, **44**, 123T (1925). See also Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.*, **69**, 277 (1926). Waltner, K., *Magyar Orvosi Arch.*, **28**, 6, 13, 19 (1927); *Chem. Abs.*, **21**, 1480 (1927), claimed to have "activated" tyrosine, but this was disproved by Kon, S. K., and Moore, T., *Biochem. J.*, **21**, 1368 (1927) and later by Waltner himself, *Magyar Orvosi Arch.*, **29**, 151 (1928); *Chem. Abs.*, **22**, 4155 (1928).

² Hess, A. F., Weinstock, M., and Hellman, F. D., *Proc. Soc. Exptl. Biol. Med.*, **22**, 76 (1924).

^{2a} This term must not be confused with photochemical activation in the sense of excitation of a molecule to a higher energy level.

³ Steenbock, H., and Black, A., *J. Biol. Chem.*, **64**, 263 (1925).

⁴ Bills, C. E., *J. Biol. Chem.*, **66**, 451 (1925).

⁵ Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181 (1925).

Rosenheim⁶ verified the activatability of cholesterol and, with Webster,⁷ obtained a fraction of the irradiated material which protected against rickets when given in daily doses of but 0.01 mg.

Attempts were soon made to activate various derivatives of cholesterol and analogous compounds. Hottinger⁸ found that the salts of the bile acids could not be rendered antirachitic by irradiation. Although he obtained no indications of growth-promoting power in irradiated solutions of cholesterol acetate or palmitate, Hottinger stated that cholesterol oleate can be made antirachitic and Bills and McDonald⁹ found the same to be true of the acetate, isobutyrate and benzoate although not of cholesterol ethers. They established that the double bond of cholesterol must remain intact for the change to occur, although the alcohol group may be esterified. Schlutz, Ziegler and Morse¹⁰ definitely eliminated the oxidation products of cholesterol as α - and β -cholesteryl oxides, hydroxy-cholesterol, and α -cholestantriol as either the vitamin or its precursor. They made the suggestion that the provitamin of cholesterol might have been, both in their own experiments and those of others, some difficultly removable impurity rather than cholesterol itself. Epicholesterol cannot be rendered antirachitic by irradiation.¹¹

According to Hume and Smith,¹² the sterols obtained from the small Siak-illipe nut can be activated. Hess and Anderson¹³ found that irradiation makes α -sitosterol strongly antirachitic, but does not affect the β - and γ -sitosterols.¹⁴

Von Euler, von Euler and Rydbom¹⁵ found it possible to activate the sterols extracted from dried red blood cells.¹⁶ They also observed the possibility of activating the phosphate and phosphite esters of sterols. Coprosterol, being an isomer of dihydrocholesterol and therefore lacking double bonds, cannot be activated.¹⁷ The same is true of cerevisterol from yeast.¹⁸

Early Views as to the Change Involved. Certain features of the mechanism of the irradiation process were made clear even in this early phase of the investigations. No change in the elementary composition of cholesterol could be detected by Hess, Weinstock and Sherman¹⁰ after an hour of irradiation. This was an essentially correct observation which did not receive sufficient credence, since it was thought that combustion methods might not detect a slight amount of change in the composition of the highly active, but unisolated product of the irradiation. Windaus,²⁰ however, made the suggestion that

⁶ Rosenheim, O., *Lancet*, I, 1025 (1925); see also Kramer, B., Shear, M. J., and Shelling, D. H., *J. Biol. Chem.*, 71, 213, 221 (1926).

⁷ Rosenheim, O., and Webster, T. A., *Biochem. J.*, 20, 537 (1926).

⁸ Hottinger, A., *Z. Kinderheilk.*, 43, 8 (1927); *Chem. Zentr.*, II, 2036 (1928), *Chem. Abs.*, 21, 3219 (1927).

⁹ Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, 72, 13 (1927).

¹⁰ Schlutz, F. W., Ziegler, M. R., and Morse, M., *J. Biol. Chem.*, 73, 209 (1927).

¹¹ Marker, R. E., Kamm, O., Oakwood, T. S., and Laucius, J. F., *J. Am. Chem. Soc.*, 58, 1948 (1936).

¹² Hume, E. M., and Smith, H. H., *Biochem. J.*, 20, 340 (1926).

¹³ Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, 74, 651 (1927).

¹⁴ For the irradiation of anhydrous lanolin, see Bernhard, A., and Dreker, I. J., *J. Biol. Chem.*, 93, 1 (1931); Töpelmann, H., and Schuknecht, W., *Z. Vitaminforschung*, 4, 111 (1935); *Chem. Abs.*, 29, 5596 (1935); Schiellich, M., and Pallaske, G., *Deut. Med. Wochenschr.*, 61, 957 (1935); Zurukzoglu, S., and Mündel, O., *Z. Vitaminforschung*, 6, 125 (1937); *Chem. Abs.*, 31, 5446 (1937).

¹⁵ von Euler, H., von Euler, B., and Rydbom, M., *Arch. Med. Skand.*, 68, 371 (1928); *Chem. Abs.*, 22, 4591 (1927).

¹⁶ Even cholesterol or lipins from the snail can acquire antirachitic properties, Mouriquand, G., and Leulier, A., *Compt. rend.*, 188, 1701 (1929).

¹⁷ Rosenheim, O., and Webster, T. A., *Biochem. J.*, 20, 537 (1926).

¹⁸ Honeywell, E. M., and Bills, C. E., *J. Biol. Chem.*, 99, 71 (1932).

¹⁹ Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, 66, 145 (1925).

²⁰ Windaus, A., and Hess, A., *Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl.*, 175 (1926); *Chem. Abs.*, 22, 256 (1928).

the activation might involve a stereoisomerization to *allo*-cholesterol, a suggestion which proved incorrect. The melting point of a sample of cholesterol which melted sharply at 146°C. was altered²¹ by irradiation so that it melted over a range of about 20°C. Some of its color reactions, notably the Whitby test, became negative.

Oxygen was not essential to the conversion, since Hess, Weinstock and Sherman²² showed that it could be effected by irradiation under nitrogen. Contradictory reports by Tiede and Reyher in the case of milk²³ may have been due to their reliance upon odor and taste rather than an actual test of potency. Hess, Weinstock and Sherman²⁴ believed an active fraction from irradiated cholesterol to be soluble in liquid ammonia. Attempts by these authors to fractionate the altered material from unchanged cholesterol by recrystallization methods with alcohol as solvent²⁵ were unsuccessful; a gradual loss of the antirachitic activity occurred. Nitzescu, Popoviciu²⁶ and Denes-Goetz claimed to have attained some degree of concentration by such methods.

A method which proved extremely fruitful was introduced by Nelson and Steenbock.²⁷ It consisted in the precipitation of the unaltered cholesterol as a molecular compound with digitonin, a much used method in sterol chemistry. The antirachitic factor was found not to be precipitated by this reagent. The method is employed quantitatively for determining the extent to which the cholesterol has been altered during a given irradiation. The difference between the amount of sterol treated and that which can be recovered by digitonin precipitation represents the amount which has been photochemically altered. Cholesterol liberated from the digitonin precipitate was found to be capable of activation on renewed irradiation. Similar results were obtained by Hess, Weinstock and Sherman.²⁸

On prolonged irradiation the antirachitic activity first produced is destroyed. This process is irreversible.²⁹ Prolonged irradiation of cod-liver oil deprives it of its antirachitic vitamin. This, Adam³⁰ suggested, might be due to an oxidative cleavage with the production of an acid, the iodine number being inversely proportional to the time of irradiation. Hottinger³¹ also observed that the antirachitic material is irreversibly destroyed by heating it at 150 to 200°C. and partially so at 100 to 120°C. Bills and Brickwedde³² found that greater activity could be attained by irradiating cholesterol at liquid air temperature than at room temperature. Cholesterol solutions in oils irradiated in oxygen

²¹ Von Euler, H., Myrbäck, K., and Karlsson, S., *Z. physiol. Chem.*, **157**, 263 (1926).

²² Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

²³ Tiede, E., and Reyher, P., *Naturwiss.*, **14**, 741 (1926).

²⁴ Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **70**, 123 (1926).

²⁵ Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

²⁶ Nitzescu, I. I., Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9**, 126 (1927); *Brit. Chem. Abs.*, **1927A**, 487.

²⁷ Nelson, E. M., and Steenbock, H., *J. Biol. Chem.*, **64**, 299 (1925).

²⁸ Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **70**, 123 (1926). See also Nitzescu, I. I., Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9**, 126 (1927); *Chem. Abs.*, **21**, 487 (1927). Occasional inaccurate statements imply that the vitamin may be precipitated by digitonin, e.g., Beumer, H., *Klin. Wochschr.*, **5**, 1952 (1926). Thus Hess, A. F., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 169 (1925) believed irradiated cholesterol to delay the hemolytic action of digitonin by binding it more readily than does cholesterol. See also Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.*, **II**, 2036 (1928); *Chem. Abs.*, **21**, 3219 (1927).

²⁹ Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

³⁰ Adam, A., *Klin. Wochschr.*, **5**, 1648 (1926); *Chem. Abs.*, **21**, 119 (1927).

³¹ Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.*, **II**, 2036 (1928); *Chem. Abs.*, **21**, 3219 (1927).

³² Bills, C. E., and Brickwedde, F. G., *Nature*, **121**, 452 (1928).

exhibit a change in dielectric constant, according to Ellinger.³³ This is attributed to an oxidation process rather than to the formation of the antirachitic substance since it does not occur during irradiations in the absence of air, under which conditions the vitamin can be formed. Bills and McDonald³⁴ succeeded in obtaining a slight degree of activation of cholesterol without irradiation by treatment with a certain fuller's earth called floridin.

ULTRAVIOLET ABSORPTION STUDIES AND ERGOSTEROL AS A PROVITAMIN

Studies of the alterations of the absorption spectra of sterols during the formation of vitamin D directed attention to ergosterol, a difficultly removable contaminant of cholesterol as the precursor.³⁵ Von Euler³⁶ had found that the ability of various oils to be converted into the vitamin did not parallel their cholesterol content. It has subsequently been demonstrated that the important contaminant of cholesterol is not predominantly ergosterol, but rather the spectroscopically indistinguishable 7-dehydrocholesterol.

It was first shown by Hess and Weinstock³⁷ that although the spectrum of dihydrocholesterol, which cannot be activated, remained unaltered during its irradiation, that of cholesterol underwent a series of changes. Irradiation for about an hour decreased the absorption by the cholesterol, but prolonged irradiation had the opposite effect. After 17 hours, the material had become somewhat yellow in color and melted at a lower temperature, and after 30 hours it was opaque to both the ultraviolet and blue rays. Schlutz and Morse³⁸ made the premature suggestion that the early disappearance of the absorption bands of cholesterol might be taken as an index of the potency attained, thus avoiding the necessity of prolonged animal experiments. Subsequent developments, however, showed the spectrographic changes to be extremely complicated.

Soon, however, other workers in three laboratories showed that some of the absorption bands exhibited by cholesterol were really due to an impurity. Rosenheim and Webster³⁹ showed that when the cholesterol had been purified through the dibromide it could no longer be made antirachitic by irradiation. The usual methods of purification, however, did not remove the impurity which is capable of producing the vitamin on irradiation. This is an instance of a peculiar difficulty inherent in the chemistry of the sterols in general. These substances have a tendency to form loose associations with each other, with their derivatives, and with other compounds, notably the bile acids, which renders it very difficult to obtain pure compounds by even many recrystallizations. Heilbron, Morton and Kamm⁴⁰ by fractional crystallization of cholesterol from ethyl acetate, concentrated a substance in the least soluble fraction which had three well-defined absorption bands at 2930, 2800 and 2690A. These

³³ Ellinger, P., *Arch. expil. Path. Pharmacol.*, **122**, 238 (1927); see also Remezov, I., *Biochem. Z.*, **248**, 256 (1932); **250**, 560 (1932); Yeremenkow, N. P., *Arch. sci. biol. (U.S.S.R.)*, **37**, 509, 542 (1935); *Chem. Abs.*, **30**, 6021, 7041 (1936).

³⁴ Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **68**, 821 (1926); **72**, 1 (1927); see also Yoder, L., *Science*, **80**, 385 (1934).

³⁵ This work has been reviewed by Loofbourow, J. R., *Bull. Basic. Sci. Research*, **3**, 101, 201 (1931); **4**, 59 (1932).

³⁶ von Euler, H., *Arch. Kemi Mineral Geol.*, **9**, 28 (1925).

³⁷ Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181, 193 (1925); Hess, A. F., Weinstock, M., and Helman, F. D., *Proc. Soc. Exptl. Biol. Med.*, **22**, 227 (1924-5).

³⁸ Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925); Schlutz, F. W., and Ziegler, M. R., *J. Biol. Chem.*, **69**, 415 (1926).

³⁹ Rosenheim, O., and Webster, T. A., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **20**, 537 (1926).

⁴⁰ Heilbron, I., Morton, R. A., and Kamm, E. D., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **24**, 78 (1927).

disappeared when the substance was irradiated, either in the solid state or in solution in alcohol or ether. At Göttingen, Pohl⁴¹ found a sample of cholesterol which exhibited an inflection at about 2700A, a peak at about 2800 and an inflection at about 2900A to be altered by irradiation by a magnesium spark in such a way as to increase the transmission between 2500 and 3100A. As great a change could be produced in ten minutes with a magnesium spark with strong lines between 2800 and 2850A as could be obtained with the unfiltered mercury arc in an hour. By subtraction of the absorption curve obtained after an irradiation of twenty minutes from the original absorption curve of the sample there was obtained an absorption curve of the material which had been altered by the irradiation. This curve was subsequently shown to correspond to the absorption curve of ergosterol.⁴² The decrease in extinction values at 2800A, indicated that, had the original absorption band truly belonged to cholesterol, about half of the sample must have been altered during the irradiation. Actually, however, at least 99.5 per cent of the original cholesterol could be recovered unchanged after such a treatment. The absorption which is altered during the irradiation must, therefore, be that of a contaminant. From the extinction values of ergosterol, Pohl concluded that his original cholesterol samples had been contaminated with this sterol to the extent of about one in 6000. Bills, Honeywell and McNair⁴³ found the ergosterol bands shown by samples of cholesterol could be made to disappear by treatment with charcoal. The original samples had been contaminated to the extent of about 1.2 parts per thousand. The disappearance of the ergosterol bands of ordinary cholesterol and bromide-purified cholesterol to which ergosterol had been added, during treatment with a permanganate solution was so similar as to afford further evidence that ergosterol is at least a contaminant of cholesterol. Rosenheim and Webster⁴⁴ estimated the intensity of the absorption by ergosterol to be from 1500 to 2000 times that of brain cholesterol. By irradiating ergosterol itself rather than cholesterol they soon obtained far more potent preparations than those obtainable by the irradiation of cholesterol. Similar results have been reported for the case of the zymosterol of yeast.⁴⁵

Ergosterol is a sterol first isolated by Tanret from ergot, a fungus on rye, a material which itself is said to have a definite antirachitic action on dogs.⁴⁶ It is also present in yeast, and is apparently present in both animal and plant cells as a contaminant of their respective sterols. Its occurrence in such vegetable oils as that of the peanut has been reported by Morton, Heilbron and Kamm⁴⁷ and it was detected in animal skin (pig) by Rosenheim and Webster.⁴⁸ The structures of cholesterol and ergosterol are given below. There remains one doubtful point in the latter. The formula given is that of Windaus, in which one double bond is placed in the C_7-C_8 position. Heilbron places it in the C_8-C_9 position. This would mean that the two double bonds in Ring B are not in conjugation. Against this Dimroth and Traut-

⁴¹ Pohl, R., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 142 (1926).

⁴² Pohl, R., *Naturwiss.*, 15, 433 (1927); *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 185 (1927).

⁴³ Bills, C. E., Honeywell, E. M., and McNair, W. A., *J. Biol. Chem.*, 76, 251 (1928); Bills, C. E., *Ibid.*, 66, 451 (1925).

⁴⁴ Rosenheim, O., and Webster, T. A., *Lancet*, I, 306 (1927); *Biochem. J.*, 21, 381 (1927).

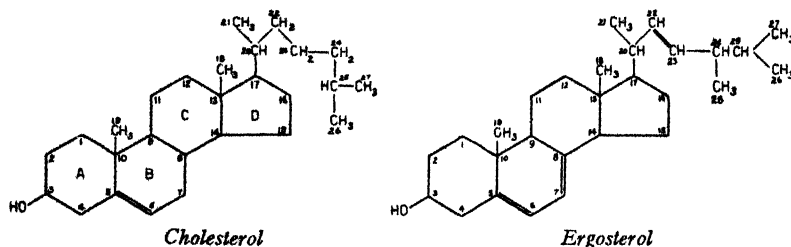
⁴⁵ Fabre, R., and Simonnet, H., *Compt. rend.*, 188, 1312 (1929); Hume, E. M., Smith, H. H., and Smedley-MacLean, L., *J. Soc. Chem. Ind.*, 47, 537 (1928); Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, 74, 652 (1927).

⁴⁶ Mellanby, E., Surie, E., and Harrison, D. C., *Proc. Physiol. Soc., J. Physiol.*, 65, xxix (1928); *Chem. Abs.*, 23, 1163 (1929); *Biochem. J.*, 23, 710 (1929).

⁴⁷ Morton, R. A., Heilbron, I., and Kamm, E., *Biochem. J.*, 21, 1279 (1927).

⁴⁸ Rosenheim, O., and Webster, T. A., *Biochem. J.*, 21, 389 (1927).

mann⁴⁹ point out that such a structure would not be expected to give the characteristic absorption bands of ergosterol. They also show that ergostatriene, the unsaturated parent hydrocarbon of ergosterol, and 7-dehydrocholestene each have the same absorption spectrum as ergosterol, so that the hydroxyl group at position 3 does not influence the absorption.⁵⁰



Various related compounds have been irradiated, with negative results.⁵¹ Among these were Reindel's isoergosterol⁵² and the fungisterol of ergot.⁵³ Positive results claimed by Windaus in the case of digitaligenin,⁵⁴ which like ergosterol contains three double bonds, could not be confirmed by Rosenheim and Webster. The absorption spectrum of ergosterol is given in Figure 152. During the irradiation of ergosterol, some of its color reactions suffer alteration. In the Meesemaeker reaction,⁵⁵ the addition of acetic anhydride and anhydrous zinc chloride to a chloroform solution of ergosterol produces a rose color which changes to a stable green. After irradiation of the ergosterol solution, however, only the green color results.⁵⁶

INFORMATION YIELDED BY STUDIES OF THE CHANGES IN ULTRAVIOLET ABSORPTION OF ERGOSTEROL DURING IRRADIATION.

Many of the earlier papers dealing with the conversion of ergosterol into an antirachitic product relied chiefly upon the evidence yielded by the changes in absorption for conclusions as to the nature of the processes occurring. The first object was to obtain from such studies a clear indication of the absorption spectrum of the antirachitic substance. The results were extremely confusing and led various workers successively to consider three different absorption maxima as characterizing the vitamin. It was at first believed to have a prominent band at about 2450A, but this was subsequently shown to characterize instead overirradiated solutions of but little antirachitic activity. Then it was thought that a band near 2800A, with greater extinction coefficients than that of ergosterol, might represent the vitamin; but this was later found in error due to the fact, since demonstrated in the laboratory of Windaus, that a number of reactions are involved in the formation of the vitamin, each

⁴⁹ Dimroth, K., and Trautmann, G., *Ber.*, **69B**, 669 (1936).

⁵⁰ See, however, Heilbron, I. M., *J. Soc. Chem. Ind.*, **55**, 129 (1936).

⁵¹ Rosenheim, O., and Webster, T. A., *Biochem. J.*, **22**, 762 (1928).

⁵² Reindel, F., Walter, E., and Rauch, H., *Annalen*, **452**, 34 (1927).

⁵³ Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).

⁵⁴ Windaus, A., *Z. angew. Chem.*, **40**, 697 (1927); Windaus, A., and Holtz, F., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 217 (1927); *Chem. Abs.*, **22**, 3910 (1928).

⁵⁵ Meesemaeker, R., *Compt. Rend.*, **190**, 216 (1930); *Brit. Chem. Abs.*, **A**, 477 (1930).

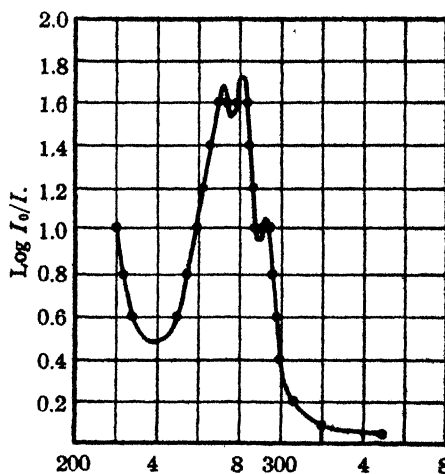
⁵⁶ See also Häussler, E. P., and Brauchli, E., *Helv. Chim. Acta*, **12**, 187 (1929) for the effects of irradiation on the Tortelli and Jaffe reaction.

attended by absorption changes and in part occurring simultaneously. Finally, it has been established that the antirachitic material has an absorption band in the region of 2650Å.

Pohl⁸⁷ found that irradiation of ergosterol solutions with a magnesium spark for 25 minutes caused a fading of the 2800Å band of ergosterol resulting in a change in the absorption spectrum. By subtracting the original curve from that after irradiation, Pohl was led to conclude that the true absorption spectrum of the vitamin would be characterized by a band with a maximum at 2450Å. Similar conclusions were reached independently by Morton, Heilbron and Kamm,⁸⁸ who observed that the band at 2470Å disappeared on prolonged irradiation, just as vitamin D was known to be destroyed. Their assays, carried out by the fecal alkalinity method, were not sufficiently accurate to demonstrate that overirradiation had already occurred when the 2470Å band appeared. Confirmation of the general course of the spectographic changes was afforded by Van Stolk, Dureuil and Heudebert.⁸⁹

FIGURE 152.

Absorption of Ergosterol (Marshall and Knudson, *Journal American Chemical Society*).



The erroneous correlation of the band near 2470Å with that of the vitamin led to the use of the appearance of this band as a criterion of suitable time and conditions of irradiation in commercial preparations of irradiated ergosterol introduced in Europe, and which were therefore actually overirradiated so that they contained toxic products. (See Chapter 38).

Bills, Honeywell and Cox⁹⁰ presented a curve for the potency of a 1 gm. per liter alcoholic solution of ergosterol after various times of irradiation in 2 cm. quartz cells directly in contact with the window of a water-cooled Kromayer lamp. Comparison of this curve with the absorption spectra obtained after various times of irradiation showed that the maximum potency had been attained and passed before the band near 2450Å had become prominent, and that by the time it had reached its maximum, the potency had been largely destroyed. In a repetition of the work during which air was admitted into the cell, this band developed and faded more rapidly, but the activation curve was essentially the same as before. They believed that although oxidation might play a part in the destruction of the 2480Å band, it was probably not concerned in the formation of the vitamin. They stated that the band at 2480 occurs also in the spectrum of an isoergosterol of Reindl, Walter and Rauch.⁹¹ Rosenheim

⁸⁷ Pohl, R., *Naturwiss.*, **15**, 433 (1927)

⁸⁸ Morton, R. A., Heilbron, I. M., and Kamm, E. D., *J. Chem. Soc.*, 2000 (1927); see also Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).

⁸⁹ Van Stolk, D., Dureuil, E., and Heudebert, *Compt. rend.*, **187**, 854 (1928); *Chem. Abs.*, **23**, 1166 (1929).

⁹⁰ Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **80**, 557 (1928).

and Webster also made it clear⁸² that the 2450A band is characteristic of a degradation product and not of the vitamin. Tixier⁸³ concluded that the time when the absorption at 2537A is a maximum does not correspond to the time at which the antirachitic potency is greatest.

Smakula⁸⁴ continued the work of Pohl but used only very short irradiation periods⁸⁵ and excluded oxygen which he thought might alter some of the irradiation products. His observations eliminated the 2470A band as the vitamin absorption. He suggested that the true vitamin bands might be located near 2600 and 2900A.

Webster and Bourdillon⁸⁶ believed, as did Smakula, that during the early periods of irradiation, the absorption increases in a manner suggestive of the possibility that the vitamin has a band near 2800A. However, after the removal of unaltered ergosterol by digitonin precipitation, the absorption curve of the remaining solution showed less absorption than did that of ergosterol except in the region of wave-lengths longer than 3000A. This apparent decrease in absorption in the regions 2800 to 2900 they attributed to the simultaneous formation of some product without either absorption or antirachitic activity. Their belief that the vitamin absorbed at 2800A was founded in part upon the fact that a reirradiation of active preparations by filtered rays free from wave-lengths shorter than 2600A destroyed their antirachitic activity.

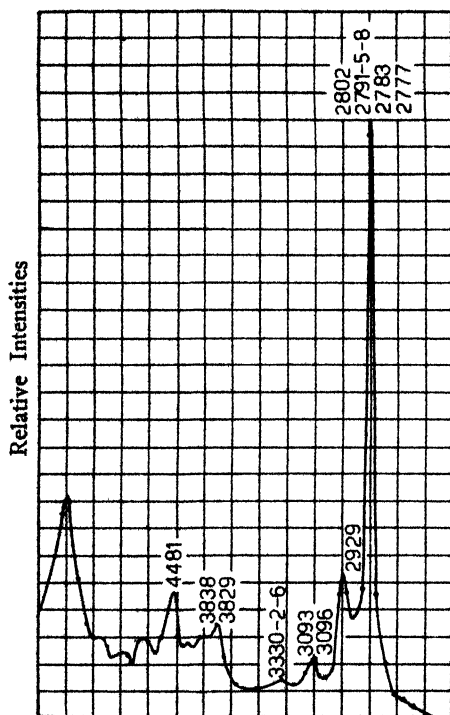


FIGURE 153.

Energy Distribution of Magnesium Spark (From Marshall and Knudson, *Journal of the American Chemical Society*).

⁸² For further discussion of early work on the significance of this band, see Morrison, R. R., and Clark, L. H., *Brit. J. Radiology*, **2**, 307 (1929); *Chem. Abs.*, **23**, 5221 (1929); Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10**, 1100 (1928); *Chem. Abs.*, **23**, 421 (1929); *Compt. rend. soc. biol.*, **99**, 193 (1928); *Chem. Abs.*, **22**, 3438 (1928); *Compt. rend.*, **188**, 424 (1929); *J. Pharm. chim.*, **9-10**, 331 (1929); Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929); Castille, A., and Ruppel, E., *Bull. Acad. Roy. Med. Belg.*, 799 (1929).

⁸³ Rosenheim, O., and Webster, T., *Biochem. J.*, **22**, 1223 (1928).

⁸⁴ Tixier, G., *Compt. rend.*, **188**, 206 (1929).

⁸⁵ Smakula, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, **49** (1928); *Chem. Abs.*, **23**, 1157 (1929).

⁸⁶ See also Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929).

⁸⁷ Webster, T. A., and Bourdillon, R. B., *J. Soc. Chem. Ind.*, **47**, 1060 (1928); *Biochem. J.*, **22**, 1223 (1928).

The importance of a band at 2650A was first emphasized by Reerink and van Wijk.⁶⁷ These workers studied separately the effects of irradiation by wave-lengths longer than about 2750A and by shorter wave-lengths. Their long wave-lengths were obtained by the use of either a mercury arc or a magnesium spark (Fig. 153), in either case filtered through a half cm. of a 10-per cent benzene solution. Hexane solutions of ergosterol were irradiated in quartz containers completely filled which had been cooled in solid carbon dioxide and evacuated by a high-vacuum pump, before sealing off. During the first fifteen minutes of irradiation there was an increased absorption throughout a large portion of the spectrum, later followed by a lessening of the absorption in the long wave-length region with but little change in the shorter wave-length region. The maximum at 2820A diminished from the beginning but that at 2715A increased at first. The nature of the changes in the absorption

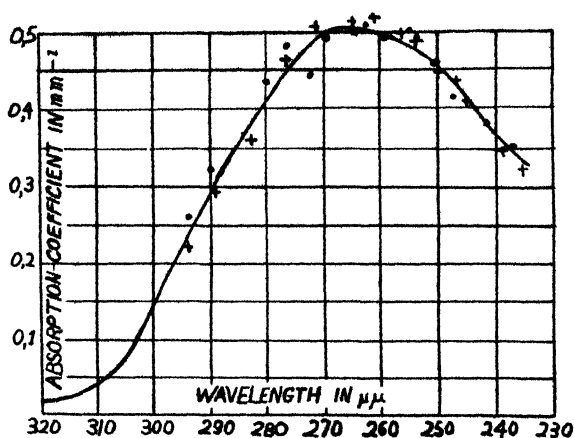


FIGURE 154. Absorption of Product L of Reerink and van Wijk (*Biochemical Journal*).

curves suggested that several substances were formed successively. By the use of very short irradiation periods they found an early formed product to have the absorption curve obtained by the difference method of Pohl and Smakula indicated in Fig. 154. This was called product L. This absorption could be confirmed as that of the residue after removal of the unchanged ergosterol by digitonin precipitation if special precautions were taken to exclude oxygen. The single broad absorption band with its maximum near 2650A was attributed to the vitamin. There were some indications that it could be obtained as crystals at low temperatures. These authors believed that for irradiation periods up to about fifteen minutes, when 50 per cent of the ergosterol had been altered, practically all of the product consisted of the vitamin. After longer irradiation periods, 45 minutes to forty hours, larger quantities of secondary products with less absorption near 2700A appeared. After 25 hours of irradiation the ergosterol bands at 2800 and 2900A had practically disappeared and a broad band between 2400 and 2500A became prominent. Animal experiments by Everse

⁶⁷ Reerink, E. H., and van Wijk, A., *Biochem. J.*, 23, 1294 (1929); *Proc. Acad. Sci. Amsterdam*, 32, 845 (1929); *Chem. Abs.*, 24, 1408 (1930); *Nederland, Maandschr. Geneesk.*, 17, 1 (1930); *Chem. Abs.*, 24, 4534 (1930); *Nature*, 122, 648 (1928).

and van Niekerk⁶⁸ indicated the antirachitic activity to be closely correlated with the amount of this substance *L* calculated to be present from the spectrographic observations. Minimum daily doses of 100 γ of the most potent products (assumed from the degree of transformation of the ergosterol indicated by digitonin precipitation to be 50 per cent vitamin) cured rachitic rats in two weeks.

In their short wave-length experiments they employed a mercury argon source, operated to give chiefly an intense mercury resonance line at 2537A, with two filters, which transmitted most of the energy of this line. One, a 2-cm. column of saturated chlorine vapor at 6 atmospheres, absorbed the longer wave-lengths. The other, a 0.5-cm. column of 0.5-per cent aqueous potassium nitrate absorbed wave-lengths shorter than 2410A. Under these conditions, it seemed that from the start secondary reactions occurred. The general change seemed to be at first an increased absorption throughout the entire spectrum, followed by a gradual diminution culminating in practically complete transparency after 330 minutes. The ratios of the extinction coefficients of the 14-, 60- and 135-minute samples appeared independent of the wave-length within a wide range and indicated that these curves are representative of various concentrations of a substance *S*. This was marked by absorption at 2800A. Upon further irradiation, it was converted into a practically transparent product. From a comparison of the absorptions of *S* and that of *L* of the long wave-length irradiation experiments, it was concluded that early in the irradiations by short wave-lengths substance *L* is mainly formed with but little of *S*. But the rate of destruction of *L* by the 2537A line was much greater than that of *S* so that the concentration of *L*, assumed to be the vitamin, never made a high percentage of the materials present during the short wave-length irradiation. It was suggested that the product of Webster and Bourdillon may have contained the *S* substance and that this was responsible for their absorption results.

That divergent results are obtainable by the use of different wave-lengths was also indicated by the work of Griffith and Spence,⁶⁹ who employed a monochromator. Ergosterol irradiated by wave-lengths 2650A and shorter, when fed at a level of 0.01 mg. per day, failed to cure rats in two weeks but was effective in four weeks. Samples irradiated with rays in the range 2650 to 3130A cured in two weeks. Samples irradiated by still longer wave-lengths did not become antirachitic.

In subsequent work by Bourdillon, Fischmann and Jenkins,⁷⁰ it was shown that solutions of ergosterol of low concentration required shorter periods of irradiation to attain the maximum absorption at 2800A than those of higher concentrations. This is in agreement with the results of other photochemical changes outlined in the second section of this book. They also showed that when the radiations shorter than 2650A were filtered out the formation of the substance absorbing at 2800A was lessened, as had been shown by the Dutch workers, in the case of their substance *S*. They later agreed⁷¹ that the substance with marked absorption between 2700 and 2800A is not the vitamin. They were able to obtain preparations of high potency but low absorption at 2800A. Lahousse and Gonnard⁷² agreed in general with the results of Reerink and van Wijk. They found in the best products absorption at 2570 and probably

⁶⁸ See Everse, J. W. R., and van Niekerk, J., *Nederland Tijdschr. Geneesk.*, **75**, 1101 (1931); *Chem. Abs.*, **26**, 1010 (1932).

⁶⁹ Griffith, H. D., and Spence, K. C., *Brit. J. Actinotherapy*, **3**, 69 (1928).

⁷⁰ Bourdillon, R. B., Fischmann, C., and Jenkins, R., *Proc. Roy. Soc.*, **104B**, 561 (1929).

⁷¹ Bourdillon, R. B., Jenkins, R., and Webster, T. A., *Nature*, **125**, 625 (1930).

⁷² Lahousse and Gonnard, *J. phys. radium*, (6) **10**, 114S (1929).

also at 2690A but did not regard this product as the pure vitamin. It was also shown that even the substance *L* of Reerink and van Wijk was not a pure compound, two or more products being produced, probably in the same ratio in its formation. Some doubt was cast for a time upon the view that the vitamin has absorption at 2650A by the work of Ender,⁷³ who claimed that a very potent concentrate of the natural vitamin from tuna fish liver oil showed no selective absorption, a claim which has recently been shown erroneous.

Reerink and van Wijk⁷⁴ also observed that during the long-wave irradiation of ergosterol the optical rotation showed a linear dependence on the degree of transformation of the ergosterol. This they regarded as supporting the view that under their conditions but one product, the vitamin, is formed from ergosterol. This contrasted with the view of Askew, Bourdillon, Bruce, Jenkins and Webster,⁷⁵ who had obtained small amounts of a crystalline product with absorption maximum at 2680A, that the effect of long-wave irradiation is to produce simultaneously two substances, only one being the vitamin. Van Wijk, Reerink and Mörikofer⁷⁶ believed from absorption studies alone that the vitamin was more completely destroyed by prolonged exposure to sunlight than to the long-wave ultraviolet rays of the filtered mercury arc, a result they attributed to a difference in the distribution of energy from the two sources. Windaus⁷⁷ pointed out that long exposures to the magnesium spark are required to over-irradiate the vitamin, which he found to have a negative optical rotation and, from the observations of Holtz in his laboratory, to have an absorption maximum at about 2700A. It was also clear to Windaus that five or six irradiation products, all non-precipitable by digitonin, may form during the irradiation of ergosterol.⁷⁸ Haman and Steenbock⁷⁹ believe that the absorption at 2650A cannot be used as an accurate measure of the amount of the vitamin formed since the change is so complex.

Quantum Yields. During the period in which the emphasis was upon the spectrographic changes, little attempt was made to bring the principles of photochemistry to bear upon the problem. Some, such as Schlutz and Morse,⁸⁰ crudely conceived the irradiated material to be merely a storehouse of radiant energy which was later supposed to be reëmitted within the body, producing a sort of internal irradiation. Nevertheless, a few physical chemists made attempts (somewhat premature in view of the state of knowledge of the mechanism of the processes involved) to learn something of the amounts of energy required for the conversion of ergosterol or unpurified cholesterol into the vitamin. Fosbinder, Daniels and Steenbock⁸¹ measured the ergs of the radiation 2650A required to produce a definite antirachitic potency in cholesterol and found the value to correspond to that in 3.2×10^{13} quanta. This was the energy required to produce a minimal threshold action. An attempt was made to calculate from this the least effective dose of the vitamin, the following assumptions being involved:

⁷³ Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); *Brit. Chem. Abs.*, **A**, 1340 (1933); *Chem. Abs.*, **28**, 4103 (1934).

⁷⁴ Reerink, E. H., and van Wijk, A., *Biochem. J.*, **25**, 1001 (1931).

⁷⁵ Askew, F. A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107B**, 76, 91 (1930); Bourdillon, R. B., Jenkins, R. G. C., and Webster, T. A., *Nature*, **125**, 635 (1930).

⁷⁶ Van Wijk, A., Reerink, E. H., and Mörikofer, W., *Strahlentherapie*, **39**, 80 (1930-31); *Chem. Abs.*, **25**, 3034, 5692 (1931).

⁷⁷ Windaus, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, **36** (1930); *Chem. Abs.*, **25**, 132 (1931).

⁷⁸ See also Holtz, F., *Strahlentherapie*, **34**, 637 (1929).

⁷⁹ Haman, R. W., and Steenbock, H., *Wis. Agr. Exp. Sta. Bull.*, **430**, 136 (1935); *Chem. Abs.*, **30**, 3472 (1936); cf. Fuchs, L., *Pharm. Presse Wiss.-Prakt. Heft*, **93** (1933); *Chem. Abs.*, **27**, 5478 (1933).

⁸⁰ Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925).

⁸¹ Fosbinder, R. J., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 926 (1928).

(a) that the molecular weight of the vitamin is the same as that of cholesterol, (b) that the Einstein photochemical equivalence law applies and (c), although this was not recognized to be an assumption at the time, that no other simultaneous photochemical process occurs and that there is no loss of energy in any overirradiation destroying the vitamin. The calculation indicated that the vitamin should be active in doses of 0.02γ . For the irradiation of ergosterol, the value was given as 0.06γ .⁸² Shortly after this, Coward⁸³ found the best preparation then available to give a positive result in the line test, a biological assay, in daily doses of 0.02γ , a result which appeared a remarkable confirmation of the physicochemical predictions. By extending the results to three other wave-

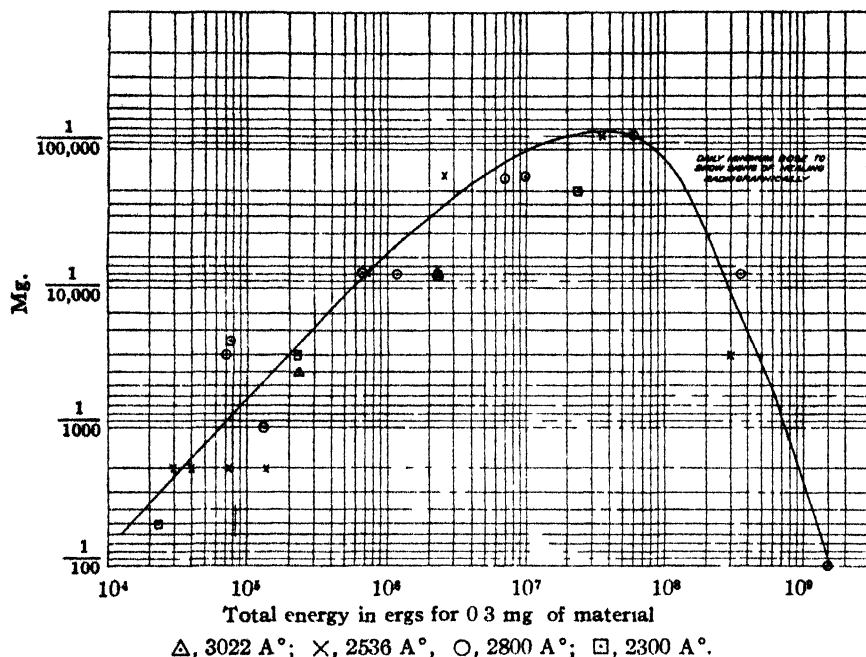


FIGURE 155. Amounts of Energy Required to Render Ergosterol Antirachitic (Marshall and Knudson, *Journal American Chemical Society*).

lengths, 2560, 2800 and 2930 Å, it was found that the results were independent of the wave length, the same dosage being arrived at in each case. In these irradiations only very short exposures were employed to eliminate the possibility of a loss of energy in overirradiation. As a result of this work the quantum efficiencies were thought to be independent of the wave-length, and, from other experiments, of the state of the ergosterol, *e.g.*, as solid or in solution (and in the latter case of the concentration of the solution). At present, it would seem very unlikely that a quantum yield of unity logically could have been assumed for photochemical reactions of such complexity occurring in condensed phases and, indeed, Kon himself has stated that the process is probably one with a low quantum yield. An approximation of the quantum yields actually

⁸² Kon, S. K., Daniels, F., and Steenbork, H., *J. Am. Chem. Soc.*, **50**, 2973 (1928).

⁸³ Coward, K. H., *Biochem. J.*, **22**, 1221 (1928).

obtained in these experiments is to be obtained by dividing the minimal dose (probably 0.03 γ) of the more recent crystalline D₂ of Windaus and others by the calculated doses of Daniels (0.06 γ). This gives a quantum yield of 0.5, still a remarkable agreement in view of the many assumptions involved. This work was extended by Marshall and Knudson⁸⁴ who plotted on log-log paper the minimum daily doses required to cure rats in three weeks which could be imparted to 0.3 mg. samples of ergosterol when irradiated by different amounts of energy at given wave-lengths. (See Figure 155). It was found that during the initial stages of irradiation the amount of the vitamin formed was directly proportional to the energy absorbed, since the minimum dose varied inversely with the ergs absorbed. For longer periods of irradiation, this relation failed, the net amount of the vitamin formed being smaller at each succeeding period until a stage was reached in which prolonged irradiation led to a loss in the vitamin previously produced. Thus these experiments yielded an independent confirmation of the results of spectrographic determinations. They calculated quantum yields of 0.3 to 0.2, based upon the potencies of the best preparations then available, those of Bourdillon and Webster. That this is greater than that of the D₂ mentioned in connection with the results of Daniels may account for the somewhat lower quantum yields of Marshall and Knudson. In two instances in which prolonged irradiations were made, the results with the 2536 and 2800Å lines appeared to be identical. This result is hard to reconcile with the observations of Reerink and van Wijk.

OTHER FEATURES OF THE IRRADIATION CHANGES

During this period a number of other observations tended to throw some light on the influence of various factors on the irradiation process. The discovery that the irradiation could be effected successfully at $-183^{\circ}\text{C}.$, a temperature at which most bimolecular reactions are markedly inhibited, suggested the likelihood that the reaction is a monomolecular process, probably an isomerization.⁸⁵ The process is markedly affected by the choice of solvent.⁸⁶ In ether, the maximum potency is about five times that which can be attained in alcohol. The maximum is reached in 27 minutes in alcohol but only after four hours in ether. The vitamin is destroyed much more slowly by overirradiation in ether. Cyclohexane as solvent is intermediate between alcohol and ether. The vitamin can be destroyed by x-rays.⁸⁷

During the early studies attempts were made to render unpurified cholesterol antirachitic by the action of x-rays. Hess and Weinstock⁸⁸ were unable in this way to alter its absorption spectrum, but Roffo and Correa⁸⁹ found that it was thereby rendered nonprecipitable by digitonin. Reinhard and Buchwald⁹⁰ found the absorption to be shifted to longer wave-lengths by x-rays or γ -rays, although the change in optical rotation was but slight. No antirachitic potency was acquired, according to Stenstrom, Lohmann and Hillstrom.⁹¹

Knudson⁹² found commercial cholesterol could be rendered antirachitic by the

⁸⁴ Marshall, A. L., and Knudson, A., *J. Am. Chem. Soc.*, **52**, 2304 (1930).

⁸⁵ Bills, C. E., and Brickwedde, F. G., *Nature*, **121**, 452 (1928).

⁸⁶ Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **92**, 601 (1931).

⁸⁷ Morrison, R. R., Peacock, P. R., and Wright, S., *Biochem. J.*, **22**, 1138 (1928); Sumi, M., *Bull. Inst. Phys. Chem. Research, (Tokyo)* **8**, 640 (1929); *Chem. Abs.*, **25**, 1875 (1931).

⁸⁸ Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181 (1925).

⁸⁹ Roffo, A. H., and Correa, L. M., *Boll. Inst. Med. Esptl.*, No. 5 (1925); *Brit. Chem. Abs.*, **A**, 523 (1929).

⁹⁰ Reinhard, M. C., and Buchwald, K. W., *J. Biol. Chem.*, **73**, 383 (1927).

⁹¹ Stenstrom, W., Lohmann, A., and Hillstrom, H. T., *Proc. Soc. Exptl. Biol. Med.*, **25**, 817 (1928).

⁹² Knudson, A., *Science*, **66**, 176 (1927); Knudson, A., and Coolidge, W. D., *Proc. Soc. Exptl. Biol. Med.*, **24**, 366 (1927).

action of cathode rays. Hieger believed that⁹⁸ cholesterol could be made activatable by x-rays only in the presence of a chlorine-containing solvent.

Ergosterol can be rendered active by cathode rays, but the activity attainable is only 0.04 that attainable by the use of ultraviolet rays.⁹⁴ That soft x-rays may be employed for the formation of the vitamin has been observed by Delaplace and Rebière⁹⁶ and by Loofbourov and Shelow.¹⁰⁰ The glow discharge has been successfully employed by Askew, Bourdillon and Webster.⁹⁷ The claim of Takamiya⁹⁹ that ozone is able to effect the production of the vitamin is apparently incorrect in view of the work to be described in a subsequent section which shows that ozone would completely destroy features of molecular structure upon which the vitamin action depends.

Even before the isolation of crystalline irradiation products, it appeared likely that the change involved in the production of the vitamin is one of isomerization. Early suggestions of a correlation between the peroxide content of anti-rachitic products and their potency⁹⁰ did not prove significant. That oxygen is not essential to the occurrence of the desired change in ergosterol is apparent from the many investigations in which it was excluded without affecting the process.¹⁰⁰ Nevertheless, it was possible before the structural formula of the sterols was as well understood as at present, to conceive of a secondary alcohol group being converted into a ketone by a migration of hydrogen atoms to some double bond.¹⁰¹ Heilbron, Morton and Sexton¹⁰² tended to favor a ketone structure for the vitamin, particularly because of the results of studies of the monomolecular spreading on water of films¹⁰³ of the irradiation products in comparison with the types of spreading exhibited by various sterol derivatives. However, many arguments were quickly marshalled against this possibility. In the first place, since ergosteryl acetate can acquire vitamin properties, it is unlikely that the hydroxyl groups can be affected.¹⁰⁴ Infrared absorption studies¹⁰⁵ indicated the persistence of the alcohol group and the non-appearance of a ketone group during the irradiation, except possibly in over-irradiated products. This was in agreement with the conclusions of Windaus and Linsert¹⁰⁶ from chemical evidence. It was stated that the optical activity changes from about -100° to $+15^\circ$ in 45 hours, but that the molecular weight remains unchanged and a free hydroxyl group remains as shown by the action of methyl magnesium iodide. Hydrogenations and perbenzoic acid titrations of the best products then available appeared to indicate that the number of double bonds remains unaltered. (This was later shown to have been in error.) This stimulated a number of

⁹⁸ Hieger, I., *Biochem. J.*, **21**, 407 (1927).

⁹⁴ Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929); see also Hoffman, R. M., and Daniels, F., *J. Biol. Chem.*, **115**, 119 (1936).

⁹⁶ Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929).

⁹⁰ Loofbourov, J. R., and Shelow, E., *Bull. Basic Sci. Research*, **3**, 47 (1931).

⁹⁷ Askew, F. A., Bourdillon, R. B., and Webster, T. A., *Biochem. J.*, **26**, 814 (1932).

⁹⁹ Takamiya, E., *Bull. Agr. Chem. Soc. Japan*, **5**, 72 (1929); *Chem. Abs.*, **25**, 536 (1931); *J. Dept. Agr. Kyushu Imp. Univ.*, **3**, 1 (1930); *Chem. Abs.*, **25**, 1877 (1931).

¹⁰⁰ Yoder, L., *J. Biol. Chem.*, **70**, 297 (1926); Schimkus, B., *Arch. Exptl. Path. Pharmacol.*, **121**, 230 (1927); *Chem. Abs.*, **21**, 2335 (1927); Rousseau, E., *Compt. rend. soc. biol.*, **99**, 1844 (1928).

¹⁰⁰ See Beard, H. H., Burke, R. E., Thompson, H. E., and Goldblatt, H., *J. Biol. Chem.*, **96**, 307 (1932).

¹⁰¹ See Windaus, A., and Linsert, O., [*Annalen*, **465**, 148 (1928)] for an early discussion of the chemical possibilities.

¹⁰² Heilbron, I. M., Morton, R. A., and Sexton, W. A., *J. Chem. Soc.*, **47** (1928); Sexton, W. A., *Biochem. J.*, **22**, 1133 (1928).

¹⁰³ Rosenheim, O., and Adam, N. K., *Proc. Roy. Soc.*, **105B**, 422 (1929); Steigmann, A., [*Kolloid Z.*, **45**, 165 (1928); *Chem. Abs.*, **22**, 3432 (1928)] favored a ketone structure because of a color test.

¹⁰⁴ Heilbron, I. M., *Brit. J. Actinotherapy*, **2**, 210 (1928).

¹⁰⁵ Shelow, E., *Bull. Basic Sci. Res.*, **3**, 175 (1931); see also Hirsch, W., and Kellner, L., *Klin. Wochschr.*, **10**, 171 (1931); *Chem. Abs.*, **25**, 2173 (1931); *Biochem. Z.*, **235**, 162 (1931).

¹⁰⁶ Windaus, A., and Linsert, O., *Annalen*, **465**, 148 (1928); Windaus, A., Westphal, K., von Wender, F., and Rygh, O., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, **45** (1920); *Chem. Abs.*, **24**, 4799 (1930); Windaus, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, **36** (1930).

investigations regarding the possible potency or activatability of the various chemically prepared isomers of ergosterol in which the positions of the double bonds are shifted, as well as that of the stereoisomers.¹⁰⁷

ISOLATION OF CRYSTALLINE IRRADIATION PRODUCTS

Attention was diverted to the study of crystalline irradiation products which were isolated about 1930. There were a few earlier observations. Jendrassik and Keményfi¹⁰⁸ claimed the isolation of a crystalline substance effective in a daily dose of 0.01 γ . This may be doubted since the product was said to exhibit no ultraviolet absorption spectrum and since the activity claimed exceeds that of the well-characterized products later obtained by others.* The first definitely characterized crystals, isolated by Windaus, Gaede, Köser and Stein,¹⁰⁹ proved to be biologically inactive as a result of over irradiation (50 hours). They could be separated into two fractions by fractional crystallization of the allophanate from benzene. As an indication of the excessive irradiation employed, they were called suprasterols I and II. Neither showed absorption of wave-lengths longer than 2500A. They were not precipitated by digitonin and were not mutually interconvertible. Suprasterol I melted at 104°C. and II at 110°C. They appeared to be triply unsaturated monohydric alcohols.

Active crystals were obtained shortly after this by Askew, Bourdillon, Bruce, Jenkins and Webster.¹¹⁰ Ergosterol in ether solution was irradiated by a mercury-vapor lamp while flowing through a quartz tube at such a rate that about 40 per cent of the ergosterol was altered. After removal of the unchanged sterol by digitonin precipitation, the solution was evaporated *in vacuo* to a dry resin. By distillation at pressures between 0.002 and 0.01 mm. there were obtained distillates which, on solution in alcohol with water added formed just opalescent liquids. These mixtures, on slow evaporation in a vacuum desiccator, gave crystals melting 113-115°C. The ultraviolet absorption of these crystals agreed with that of the substance L of Reerink and van Wijk and in several samples the absorption paralleled the biological activity. The crystals were at first thought to be a mixture of two or more very similar substances (only one of which might be the vitamin), or else mixtures of antirachitic substances of different degrees of potency.

It was shown that a product prepared by irradiation with longer wave-lengths suffered a change on subsequent irradiation by shorter wave-lengths (2100-2800A), the absorption increasing at 2800A and the antirachitic value falling. On the other hand, irradiation by long wave-lengths for fifteen minutes had but little effect on the antirachitic potency. It was suggested, from closer analysis of the results, that the inactive substance absorbing at 2800A is produced during the re-irradiation of the long wave-length product by short wave-lengths, not from the vitamin but from some other substance present, to an extent which depends

¹⁰⁷ Bills, C. E., and Cox, W. M., Jr., *J. Biol. Chem.*, **84**, 455 (1929); Bills, C. E., Cox, W. M., Jr., and Steel, G. F., *Ibid.*, **84**, 655 (1929); MacCorquodale, D. W., Steenhock, H., and Adkins, H., *J. Am. Chem. Soc.*, **52**, 2512 (1930); Hart, M. C., and Heyl, F. W., *Ibid.*, **52**, 2013 (1930); Emerson, H., and Heyl, F. W., *Ibid.*, **52**, 2015 (1930); Hart, M. C., Speer, J. H., and Heyl, F. W., *Ibid.*, **52**, 2016 (1930); Heilbron, I. M., Johnstone, J., and Spring, F. S., *J. Chem. Soc.*, 2248 (1929); Windaus, A., and Auhagen, E., *Annalen*, **472**, 185 (1929); Windaus, A., Diithmar, K., Murke, H., and Suckfüll, E., *Annalen*, **488**, 91 (1931); Cox, W. M., Jr., and Bills, C. E., *J. Biol. Chem.*, **88**, 709 (1930); Natelson, S., Sobel, A. E., and Kramer, B., *Ibid.*, **105**, 761 (1934); Natelson, S., and Sobel, A. E., *Ibid.*, **109**, 687 (1935).

¹⁰⁸ Jendrassik, A., and Keményfi, A. G., *Biochem. Z.*, **216**, 238 (1929).

* Reerink and van Wijk, it may be recalled, stated that they had evidence of crystals at low temperatures in their products.

¹⁰⁹ Windaus, A., Gaede, J., Köser, J., and Stein, G., *Annalen*, **483**, 17 (1930).

¹¹⁰ Askew, F. A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107**, 76, 91 (1930).

upon the conditions used in the first irradiation. They did not believe this to be a precursor of the vitamin but some other substance formed simultaneously with it. The simultaneous production of two products, one of which is inactive, would prevent the concentration of the vitamin produced by irradiation from ever reaching 100 per cent. Within a year they had improved the technique¹¹¹ to an extent that permitted the preparation of several grams of the crystals. In this process, it was essential that oxygen be excluded. The oxygen uptake of the irradiated products was thought to be largely due to the oxidation of products other than the vitamin for much oxygen could be absorbed without a corresponding loss of potency. Provisionally, they gave the name *calciferol* to the crystals, recognizing the possibility that they might not be a single compound. This substance melted at 123-125°C. and had $[\alpha]_{20}^{5461} = +260^\circ$. The absorption spectrum showed a maximum at 2700Å and an inflection at 2600Å indicative of a second maximum. The elementary analysis and molecular weight determination indicated the substance to be an isomer (or a mixture of isomers) of ergosterol. Partially successful esterifications indicated the presence of an alcohol group. They were then uncertain as to whether the calciferol was a product of the original irradiation or one which had been altered by the heat employed in the subsequent distillation. The purity of these calciferol crystals was questioned by Bills, McDonald, Be Miller, Steel and Nussmeier.¹¹²

Meanwhile at Göttingen crystals were also obtained and called D₁.¹¹³

The irradiation products obtained under conditions of little or no over-irradiation, after being freed from unchanged ergosterol, were allowed to react with citraconic anhydride at room temperature. That portion which had reacted was removed after three days and the solvent evaporated from the remainder. The residue could be easily recrystallized, as long needles melting at 124-5°C. and subliming in high vacuum at 135°C. They had an absorption band with a maximum at 2650-2700Å and were isomeric (composition and molecular weight) with ergosterol. The limiting antirachitic dose was 0.025γ. The crystals had a high positive rotation, in acetone or alcohol, $[\alpha]_{20}^{5461} = +171^\circ$.

Samples made by the method of Reerink and van Wijk, however, showed a specific rotation of but +30°. D₁ seemed, furthermore, different from the crystals obtained in England since after ten recrystallizations, the German product had a rotation of +159° and the English of +260°. Windaus suggested that it might be that the only change involved was a steric one leading to an increase in the spatial size of the molecule. But it was suggested that during overirradiation, the double bonds which form a conjugated system may be moved to positions further apart.¹¹⁴ The combination of the crystals with maleic anhydride indicated the presence of a conjugated double bond. At room temperature the new crystals absorbed no oxygen in twelve hours.

It was soon found, however, that neither calciferol nor D₁ represented the pure antirachitic photoisomer of ergosterol. The English workers announced that¹¹⁵ by fractional crystallization of the 3,5-dinitrobenzoate, their product

¹¹¹ Angus, T. C., Askew, F. A., Bourdillon, R. B., Callow, R. K., Fischmann, C., Philpot, J., and Webster, T. A., *Ibid.*, 108B, 340 (1931).

¹¹² Bills, C. E., McDonald, F. G., Be Miller, L. N., and Nussmeier, M., *J. Biol. Chem.*, 93, 775 (1931).

¹¹³ Windaus, A., Lüttringhaus, A., and Deppe, M., *Annalen*, 489, 252 (1931); Windaus, A., *Proc. Roy. Soc.*, 108B, 568 (1931).

¹¹⁴ For evidence for this from refractive indices, see Von Auwers, K., and Wolter, E., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 101 (1931); *Chem. Abs.*, 26, 5844 (1932).

¹¹⁵ Askew, F. A., Bruce, H. M., Callow, R. K., Philpot, J. St. L., and Webster, T. A., *Nature*, 128, 758 (1931).

had been separated into an inactive substance, pyrocalciferol, formed by the action of heat during the distillation, and the true antirachitic compound, for which they retained the name calciferol. Thus their original or "old calciferol" had been calciferol contaminated with pyrocalciferol, which is again an isomer.

Windaus and Linsert, in a brief note,¹¹⁶ announced the isolation of another compound, D₂ melting at 115-116°C. and having $[\alpha]_D = +85^\circ$ in acetone. This was obtained by the dinitrobenzoate method from D₁ which was found to consist of D₂ and an isomeric alcohol.¹¹⁷ D₂ also shows definite absorption at 2650Å. New calciferol and D₂ are identical, but the old calciferol and D₁ were not. The former had as the second material pyrocalciferol (and probably also the contaminant of D₁) and the latter had as the second component an isomeric alcohol formed from ergosterol by irradiation.¹¹⁸ This has been called lumisterol, or a sterol formed by light. The lumisterol has its absorption maximum at about 2700Å and is the substance which, on irradiation with short wave-lengths, is converted to the substance with strong absorption at 2800Å. It was readily shown that lumisterol and calciferol (D₂) in equimolar proportions would have the absorption spectrum of D₁. The English workers suggested that the substance L of Reerink and van Wijk may have been a mixture of calciferol (D₂) and one or more inactive irradiation products. It was next shown by Windaus, Dithmar and Fernholz,¹¹⁹ by titrations with perbenzoic acid, that lumisterol contains three double bonds. It has no antirachitic action and is not toxic. By irradiation in ether with the unfiltered light from a magnesium arc, in which the longer rays predominate, it is converted, in part at least, into D₂. Thus it must be a transitory intermediate product in the conversion of ergosterol into D₂. From the English observations, it would seem that, if in this process the lumisterol is irradiated by too short wave-lengths, the reaction follows a different course, producing the substance which absorbs maximally at 2800Å. That the substance which disappears when this absorption at 2800Å is produced is not the vitamin had been shown previously by Windaus and Auhagen.¹²⁰

It was not yet apparent why it was so necessary to eliminate oxygen during the irradiation since none of the products thus far described is readily attacked by it. It was believed both by Windaus and by the English group that the irradiation product attacked by oxygen is not the antirachitic material. In further studies, Windaus, von Werder, and Lüttringhaus¹²¹ isolated a substance from the treatment of the irradiation product with citraconic anhydride. Because of the rapidity with which it reacts with that reagent (much greater than D₂) it was called tachysterol. Since it reacts rapidly with oxygen also, it seems to be the product which makes the exclusion of oxygen essential. That this material must be preserved in order to secure high yields of D₂ during irradiation seems to imply that it lies in the direct line of conversion of ergosterol into D₂.¹²² Tachysterol lacks antirachitic action and is not toxic.

¹¹⁶ Windaus, A., and Linsert, O., *Annalen*, 489, 269 (1931); see also *Z. physiol. Chem.*, 203, 70 (1931).

¹¹⁷ This work has been reviewed by Lüttringhaus, A., *Chem. Ztg.*, 55, 956 (1931).

¹¹⁸ Detailed accounts of the preparation of new calciferol are given in *Proc. Roy. Soc.*, 109B, 488 (1932) and of D₂ by Windaus, A., Linsert, O., Lüttringhaus, A., and Weidlich, G., *Annalen*, 492, 226 (1932). For criticism, see Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, 96, 189 (1932). For another method of obtaining the crystals, see Sumi, M., *J. Agr. Chem. Soc. Japan*, 12, 1211 (1936); *Bull. Inst. Phys. Chem. Research (Tokyo)*, 15, 635 (1936); cf. also Francesconi, L., and Opisso, F., *Ann. chim. appl.*, 25, 124 (1935); *Brit. Chem. Abs.*, A, 857 (1935); *Chem. Abs.*, 29, 6254 (1935).

¹¹⁹ Windaus, A., Dithmar, K., and Fernholz, E., *Annalen*, 493, 259 (1932).

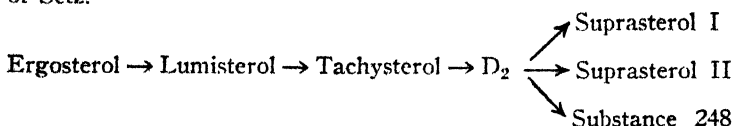
¹²⁰ Windaus, A., and Auhagen, E., *Z. physiol. Chem.*, 196, 108 (1931).

¹²¹ Windaus, A., von Werder, F., and Lüttringhaus, A., *Annalen*, 499, 188 (1932).

¹²² Inhoffen, H. H., and Hauptmann, H., [*Z. physiol. Chem.*, 207, 259 (1932)] believe that in the presence of tachysterol, D₂ becomes slightly sensitive to air.

It has a high absorption maximum at 2800 Å and further bands at 2680 and 2940 Å and is changed, in part at least, into D_2 when irradiated by the magnesium spark. It thus appears to be the substance built up by short-wave irradiation of ergosterol or of lumisterol. That it does not appear during the long-wave irradiation is probably due to the fact that it is formed only in low concentrations and immediately converted into D_2 . The use of short waves, owing to lack of absorption, could probably only very slowly convert it into D_2 .

It thus became apparent that five isomers of ergosterol are produced by irradiation and it became possible to place them in the sequence in which the transformations occur.¹²³ Slight differences in the order were suggested in these papers, the following being the sequence of changes given in the most recent paper of Setz.



The substance 248 is so called because it has an absorption maximum at 2480 Å. It may be recalled that this substance was originally mistaken for the vitamin by Pohl. It is a product of overirradiation and is not antirachitic but is toxic and sometimes called toxisterol.¹²⁴ Setz states that irradiation of any substance in the list leads to the formation of a mixture of all substances following it, but that the sequence cannot be reversed. Light of the longest wave-length, 3100 Å, capable of altering ergosterol gives rise to lumisterol after which further change is but slow. With the use of somewhat shorter wave-lengths, 2800 Å, the lumisterol stage is passed over and tachysterol is immediately produced. It is very sensitive to longer wave-lengths and is converted into D_2 . Between 3000 and 3600 Å, it absorbs more than ten times as strongly as does ergosterol. The existence of this sequence may explain why the mercury arc light, when freed by a xylene filter from rays shorter than 2800 Å, forms chiefly the vitamin and lumisterol in fairly constant proportions. The shorter rays are necessary to convert the lumisterol into tachysterol. The magnesium light, 2780 to 2800 Å, yields practically no lumisterol but chiefly tachysterol and D_2 , suggesting that the tachysterol may be formed without passing through lumisterol as an intermediate stage. Against this possibly oversimplified scheme is also the fact that on short irradiations during which but 10 per cent of the ergosterol has been altered, D_2 predominates in the mixture, although it might be expected that the first product, lumisterol, would predominate. In a product of longer irradiation (method of Reerink and van Wijk) with 50 per cent ergosterol conversion, there were found to be present about 40-50 per cent of lumisterol, 30-40 per cent of D_2 , 40-50 per cent of tachysterol, 5-10 per cent of suprasterol II and possibly also traces of suprasterol I.

By the use of a monochromator, Bowden and Snow¹²⁵ recently showed that calciferol in cyclohexane is rapidly decomposed by the wave-length 2650 Å, but is not changed by 3130 Å or longer wave-lengths. The decomposition is independent

¹²³ Windaus, A., Lüttringhaus, A., and Busse, P., *Nachr. Wiss. Göttingen, Math. Physik. Kl.* 150 (1932); *Chem. Abs.*, 27, 2180 (1933); Windaus A., von Werder, F., and Lüttringhaus, A., *Annalen*, 499, 188 (1932); Setz, P., *Z. physiol. Chem.*, 215, 183 (1933).

¹²⁴ Laquer, F., and Linsert, O., *Klin. Wochschr.*, 12, 753 (1933). Spectroscopic evidence by Dimroth indicates that ergosterol cannot form tachysterol without passing through lumisterol, *Ber.*, 70B, 1631 (1937). See also Windaus, A., *Sitzber. preuss. Akad. Wiss. Physik-math. Kl.*, No. 9-12, 104 (1937).

¹²⁵ Bowden, F. P., and Snow, C. P., *Proc. Roy. Soc.*, 115B, 261 (1934).

of the presence of air. Ergosterol in cyclohexane was not altered by the wavelength 3130A but was rapidly converted into calciferol by 2967A. With 2650A, the yield of calciferol was decreased. Thin crystals, of ergosterol were scarcely affected by 3650, 3130 or 2537A, but were rapidly transformed by 2967A.

Jendrassik¹²⁶ has claimed that ergosterol can be rendered antirachitic by irradiation with sunlight, yielding a preparation 2 per cent as potent as that produced by artificial ultraviolet sources. It has been found possible to irradiate ergosterol by ultraviolet rays which have passed through the epidermis of a day-old rat.¹²⁷

CHEMICAL CHANGES OCCURRING DURING THE IRRADIATION OF ERGOSTEROL

It has been pointed out in the preceding discussion that the various irradiation products in the sequence of changes undergone by ergosterol are all isomers. The elucidation of the constitution of each of these, established in all of the most important features, has been accomplished by the application of chemical and physical methods. Among the physical methods have been the comparison of the data on ultraviolet absorption, refractive indexes and x-ray crystal structures of these products with those of related compounds of known constitution. The chemical attack has involved the identification of oxidation products, the determination of the number of double bonds in the various products by catalytic microhydrogenation methods and by perbenzoic acid titrations, and the determination of their conjugation by the maleic anhydride reaction. The number of rings present was found by selenium dehydrogenations followed by the identification of the products. Finally, the thermal decomposition products have been studied. The details of the historical development lie beyond the scope of this discussion.¹²⁸

It was first shown that the double bond (C_{22} to C_{23}) in the side-chain is unaltered during the transformations, since ergosterol, lumisterol, tachysterol, D_2 and suprasterol I can each yield methylisopropylacetaldehyde on suitable treatment.¹²⁹ The changes must then be stereochemical or associated with the positions and stability of the double bonds within ring B of ergosterol.

Three double bonds were found present in lumisterol,¹³⁰ and studies of the oxidation products indicated them to be in substantially the same positions as in ergosterol, a result supported also by dehydrogenation experiments by Dimroth. Only a stereoisomeric change remains as a possibility.¹³¹ This was at first thought to consist in an epimerization of the hydroxyl group at position 3, but this has been shown unlikely by the observation that the unsaturated hydrocarbons produced by the dehydration of ergosterol and lumisterol by phosphoryl chloride are different.¹³² Dimroth¹³³ has shown by a comparison of the absorption spectra

¹²⁶ Jendrassik, A., *Biochem. Z.*, **252**, 205 (1932).

¹²⁷ Lucas, N. S., *Biochem. J.*, **27**, 132 (1933).

¹²⁸ For detailed reviews, see Lettré, H., *Annalen*, **511**, 280 (1934); Callow, R. K., *Sci. J. Roy. Coll. Sci.*, **4**, 41 (1934); Rosenheim, O., and King, H., *Chem. & Ind.*, 196 (1934); 699 (1935); Nicola, O., *Rev. Med. Latin-Am.*, **220**, 358 (1934); 231, 279; *Chem. Abs.*, **29**, 8075 (1935); Linsert, O., *Med. Chem. Forschungstatien I. G. Farbenind.*, **2**, 281 (1934); Rygg, O., *Tids. Kjemi. Bergvesen*, **14**, 26 (1934); Windaus, A., *E. Merck's Jahresber.*, **50**, 3 (1936); Ruzicka, L., and Goldberg, M. W., *Helv. Chim. Acta*, **18**, 434 (1935); Schmidt, O., *Ber.*, **68B**, 1658 (1935); Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 (1935); *Current Sci.*, **5**, 69 (1936); Fieser, L. F., "Chemistry of Natural Products Related to Phenanthrene," Reinhold, 2nd ed., 177 (1937); Heilbron, I. M., *Chimie et industrie*, **39**, 19 (1938); Bills, C. E., *J. Am. Med. Assoc.*, **110**, 2150 (1938).

¹²⁹ Guiteras, A., *Annalen*, **494**, 116 (1932).

¹³⁰ Dimroth, K., and Möller, F. F., *Ber.*, **68B**, 539 (1935); Heilbron, I. M., Spring, F. S., and Stuart, P. A., *J. Chem. Soc.*, 1221 (1935); Haslewood, G., and Roe, E., *J. Chem. Soc.*, 465 (1935).

¹³¹ More recent proof is due to Burawoy, A., *J. Chem. Soc.*, 409 (1937), and Heilbron, I. M., Moffet, G. L., and Spring, F. S., *J. Chem. Soc.*, 411 (1937).

¹³² See, however, Callow, R. K., and Young, F. G., *Proc. Roy. Soc.*, **157A**, 194 (1936).

of dehydrolumisterol and dehydroergosterol, and by other chemical evidence, that the change in configuration occurs at the methyl group of C_{10} .¹⁸⁴ This persists in the succeeding products as well and Dimroth attributes the inability of the irradiation products to combine with digitonin to the spatial arrangement of the methyl group at C_{10} produced in the first transformation of the series.

A most significant observation by Lettré¹⁸⁵ showed tachysterol to contain the equivalent of four double bonds.¹⁸⁶ This could result only from the opening of a ring, reducing the number of rings in the system from four to three. For a time it was believed that in the conversion of tachysterol to D_2 a fourth ring is reformed. Unfortunately, it was not possible to obtain crystalline dehydrogenation products which might yield information as to the number of rings. However, it was established that D_2 also contains four double bonds by hydrogenation and by perbenzoic acid titrations.¹⁸⁷ Müller showed that it contained three of its double bonds in a conjugated system and differed only from tachysterol in the location of these bonds. Rosenheim and King¹⁸⁸ were of the opinion that the breaking of the ring in tachysterol formation took place between $C(5)$ and $C(10)$, resulting in the unusual formation of a ten-membered ring. This view was based upon x-ray evidence of Bernal,¹⁸⁹ which appeared to indicate an essential similarity of the unit cells of all of the irradiation products, the length of the molecule not being affected by the intramolecular changes. Proof that this is incorrect and that it is the bond between positions 9 and 10 which is broken was furnished by Lettré and by Heilbron and Spring¹⁴⁰ by the study of the products of the oxidation of D_2 . In this work it was established that there must be a double bond in calciferol between positions 5 and 6. Furthermore, Windaus and Thiele by a study of certain degradation products and their maleic anhydride addition compounds located the remaining double bonds so that the structure of D_2 is that represented below.¹⁴¹

The thermal decomposition products of the D_2 , pyrocalciferol and isopyrocalciferol are formed by a process involving a ring closure,¹⁴² since the equivalent of a double bond disappears. The process occurs in such a manner as to re-form the original sterol ring system. There is evidence that a ring closure occurs also in the formation of suprasterol I by overirradiation but a different ring system, possibly containing a spirocyclopentane ring, is formed.¹⁴³

Pyrocalciferol irradiated forty hours with magnesium light in peroxide-free ether yields photopyrocalciferol, and isopyrocalciferol similarly gives a photoisopyrocalciferol. Such changes are due to the conjugated system of two double bonds between C_5 and C_6 and between C_7 and C_8 in ring B, found also

¹⁸⁰ Dimroth, K., *Ber.*, 69, 1123 (1936).

¹⁸⁴ Windaus, A., and Dimroth, K., *Ber.*, 70B, 376 (1937).

¹⁸⁵ Lettré, H., *Annalen*, 511, 280 (1934); *Angew. Chem.*, 47, 736 (1934).

¹⁸⁶ See also Kuhn, R., and Möller, E. F., *Angew. Chem.*, 47, 145 (1934).

¹⁸⁷ Müller, M., *Z. physiol. Chem.*, 233, 223 (1935); Fernholz, E., *Annalen*, 499, 198 (1932); Ahrens, G., Fernholz, E., and Stoll, W., *Ibid.*, 500, 109 (1933); Heilbron, I. M., Samant, K. M., and Spring, F. S., *Nature*, 135, 1072 (1935); Windaus, A., and Thiele, W., *Annalen*, 521, 160 (1935).

¹⁸⁸ Rosenheim, O., and King, H., *Chem. & Ind.*, 699 (1935).

¹⁸⁹ Bernal, J. D., *Nature*, 129, 277 (1932); Bernal, J. D., and Crowfoot, D., *Chem. & Ind.*, 54, 701 (1935).

¹⁴⁰ Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 (1935). The Windaus structures are corroborated by refractometric studies by von Auwers, K., [*Annalen*, 533, 255 (1938)], as well as by other recent work of Heilbron, I. M., Kennedy, T., Spring, F. S., and Swain, G., [*J. Chem. Soc.*, 869 (1938)].

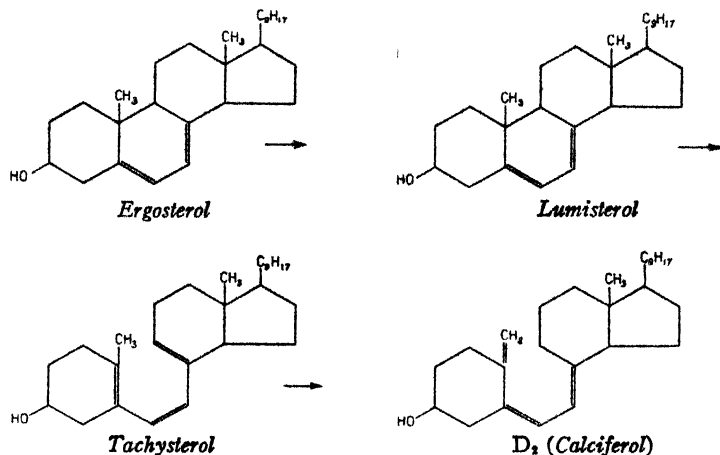
¹⁴¹ See also Heilbron, I. M., Jones, R. N., Samant, K. M., and Spring, F. S., *J. Chem. Soc.*, 905 (1936); Windaus, A., and Grundmann, W., *Annalen*, 524, 295 (1936); von Reichel, S., and Deppe, M., *Z. physiol. Chem.*, 239, 143 (1936).

¹⁴² Busse, P., *Z. physiol. Chem.*, 214, 211 (1933); Müller, M., *Ibid.*, 233, 223 (1935).

¹⁴³ Müller, M., *Z. physiol. Chem.*, 233, 223 (1935).

in ergosterol, 22-dihydroergosterol, 7-dehydrocholesterol and 7-dehydrositosterol. Pyrocalciferol and isopyrocalciferol differ from ergosterol and lumisterol in having a different steric arrangement at C_9 . The irradiation of the pyro- compounds converts the conjugated system into a system of isolated double bonds, which may again be converted by heat into the original conjugated system. No steric rearrangement occurs at C_{10} . Instead, a double linkage is shifted from ring B to ring A.

Fuchs and van Niekerk¹⁴⁴ observed that crystalline D_2 kept in air in darkness undergoes some changes involving the development of a yellow color and the loss of ultraviolet absorption. Little is yet known regarding the structure of suprasterol II or of the substance 248 (toxisterol). The structures of the various irradiation products are summarized by the following formulas:



The positions of the double bonds in tachysterol are perhaps still uncertain. If the conversion of this to vitamin D_2 is as indicated, it is conceivable that the absorption of light by tachysterol involves the liberation of atomic hydrogen which later adds on again at position 9. It would be interesting to learn whether its presence could be detected during the photochemical process by the aid of the para hydrogen conversion. Grundmann gives evidence for proposing that the double bonds in tachysterol should be placed as shown rather than in the positions 1,10; 5,6 and 7,8.¹⁴⁵

Recently, attention has been paid to the effects of irradiation on the surface pressures and surface potentials of unimolecular films of ergosterol.¹⁴⁶ The evidence indicates a change in the shape of the molecules as the irradiation proceeds. The results were attained before the structures indicated above had been determined and they have not been correlated with them as yet.

There has not as yet been achieved a direct synthesis of D_2 . Natelson and Gottfried, however,¹⁴⁷ have synthesized 4- β -phenylethylindane, the structure proposed for the calciferol nucleus.

¹⁴⁴ Fuchs, L., and van Niekerk, J., *Biochem. Z.*, **277**, 32 (1935).

¹⁴⁵ Grundmann, W., *Z. physiol. Chem.*, **252**, 151 (1938).

¹⁴⁶ Fosbinder, R. J., *Proc. Roy. Soc.* **139A**, 93 (1933); Danelli, J. F., and Adam, N. K., *Biochem. J.*, **28**, 1583 (1934).

¹⁴⁷ Natelson, S., and Gottfried, S. P., *J. Am. Chem. Soc.*, **58**, 1432 (1936).

The activation energy of the conversion of ergosterol into D_2 has recently been calculated from quantum mechanical considerations.¹⁴⁸

The activation energy sets the long wave-length limit for the conversion. If there is merely the breaking of a C—H linkage on C_{18} followed by a migration of the hydrogen atom to the carbon in position 9, the activation energy is 92.3 kcal. which agrees well with the usually accepted long wave-length limit of about 3100Å. The authors considered many other mechanisms and found the one involving the least energy of activation to require 72 kcal. which would place the long wave-length threshold at about 3950Å. The suggested mechanism does not take into account the stereochemical change involved in the formation of lumisterol. It may be that this requires a somewhat greater energy of activation and sets the observed wave-length limit.

That a longer threshold than 3100Å has not been experimentally observed may be due to the failure of ergosterol to absorb the longer wave-lengths. If this is the case and the mechanism postulated by Sherman is the actual one, it might be possible to effect the conversion in a sensitized process. There have been a number of observations of photochemical changes in ergosterol occurring in the presence of eosin and other sensitizers. The reactions observed, however, have been of an entirely different character.¹⁴⁹ The reaction is a photooxidation, in which ergosterol peroxide is produced. The reaction is inhibited by potassium cyanide. Under similar conditions, ergosteryl acetate also yields a peroxide. The peroxides are biologically inactive. In the absence of oxygen, white light in the presence of a sensitizer causes a dehydrogenation of the sterol, and there results a sparingly soluble substance, $C_{56}H_{86}O_2$, known as ergopinacol, which is biologically inert. The study of these substances played a part in the development of the structural formula for ergosterol. Rygh¹⁵⁰ found that in the presence of eosin, sunlight causes a rearrangement of ergotetraene, melting at 97°C. to an isomeric form, of slightly lower optical rotation. No peroxide was formed even in the presence of air. Windaus and Langer¹⁵¹ found that an alcoholic solution of 22-dihydroergosteryl acetate may be oxidized in the presence of eosin by a 500-watt lamp to a peroxide. The free 22-dihydroergosterol itself behaves similarly. Dimroth¹⁵² also has shown that, in alcohol, dehydrolumisterol acetate reacts with eosin in sunlight to give a so-called pinacol, but that lumisterol and pyrocalciferol do not behave in this way. Dehydroergosterol acetate and isopyrocalciferol yield the same pinacol when treated in this manner. It differs from that¹⁵³ obtained from dehydrolumisterol.

According to Montignie¹⁵⁴ sunlight does not influence the reactions of cholesterol with uranyl nitrate, silver nitrate, mercury oxide, iodoform or mercuric iodide.

OTHER ANTIRACHITIC COMPOUNDS

Windaus and Langer¹⁵⁵ made the important observation that ergosterol in which the double bond in the side chain has been saturated, i.e., 22-dihydroergos-

¹⁴⁸ Owen, J. R., and Sherman, A., *J. Am. Chem. Soc.*, **59**, 763 (1937).

¹⁴⁹ Windaus, A., Borgeaud, P., and Brunken, J., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 313 (1927); Windaus, A., and Brunken, J., *Annalen*, **460**, 225 (1928); Windaus, A., and Borgeaud, P., *Annalen*, **460**, 235 (1928); compare Meyer, K., *J. Biol. Chem.*, **103**, 607 (1933).

¹⁵⁰ Rygh, O., *Z. physiol. Chem.*, **185**, 99 (1929).

¹⁵¹ Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

¹⁵² Dimroth, K., *Ber.*, **69B**, 1123, 1631 (1936).

¹⁵³ Windaus, A., and Dimroth, K., *Ber.*, **70B**, 376 (1937).

¹⁵⁴ Montignie, E., *Bull. Soc. Chim.*, **1**, 290 (1934); *Chem. Abs.*, **28**, 5466 (1934).

¹⁵⁵ Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

terol, can also function as a provitamin, although the antirachitic activity of the irradiation product is but one-thirtieth that of D_2 . This means that the double bond in the side chain does not play a part in the sequence of irradiation, changes in the case of ergosterol. This observation was made before the evidence presented in the preceding discussion of the mechanism of the formation of D_2 .¹⁵⁶ It led to the suggestion that it might be possible to prepare an antirachitic substance from cholesterol could there first be introduced into the molecule a double bond in position 7, 8, thus rendering the molecule analogous to that of ergosterol in the features essential to the conversion. This was accomplished by Windaus, Lettré and Schenck,¹⁵⁷ who succeeded in preparing the benzoate of 7-dehydrocholesterol. The product of its irradiation even in a crude form had a high antirachitic potency, approximately half that of the product from ergosterol. This work provided a justification of the objections that had been raised by a relatively few earlier workers to the almost universally accepted view that ergosterol was the precursor of the vitamin D.

Jendrassik and Kemenyfi¹⁵⁸ had been of the opinion that a removal of the provitamin from a cholesterol preparation destroys an equilibrium between cholesterol and a provitamin leading to the conversion of more cholesterol into provitamin. They had no conception of the nature of the provitamin but suggested that it might be ergosterol. Bills, Honeywell and MacNair¹⁵⁹ maintained that samples of cholesterol contained traces of an activatable substance other than ergosterol, a view not shared by Kon, Daniels and Steenbock.¹⁶⁰ Koch, Koch and Ragins¹⁶¹ asserted that even purified cholesterol could to a slight extent be activated and that it might be made more activatable by heating it slightly above the melting point. Koch, Koch and Lemon¹⁶² concluded from spectrographic studies that ordinary cholesterol contains only about one-thousandth part of ergosterol^{162a} but was more capable of activation than could be accounted for by this ergosterol, so that some other activatable substance must be present. At the time, these views attracted relatively little attention. Yoder¹⁶³ has recently called attention to a chemical method of obtaining antirachitic material from cholesterol by means of sulfur trioxide and acetic anhydride. DeCaro¹⁶⁴ claimed the non-saponifiable fraction of lanolin acquires antirachitic properties on irradiation. Gustavson¹⁶⁵ found that the extraction of irradiated cholesterol with liquid ammonia gave a yellow resinous material a quarter of a milligram of which gave complete protection against rickets when incorporated in the McCollum rachitic diet.

The brilliant results of the ergosterol investigations diverted attention from cholesterol and it came to be rather generally believed that D_2 was identical with the vitamin from natural sources. This view was maintained until an interesting difference in the response of rachitic animals of different species to the action of the antirachitic vitamin from various sources showed the non-identity of D_2 with the natural vitamin of cod-liver oil.¹⁶⁶ Hess and Supplee¹⁶⁷ observed that chickens are regularly protected against leg weakness by the addition of

¹⁵⁶ The product has recently been isolated through the nitrobenzoate as crystalline D_4 , Windaus, A., and Trautmann, G., *Z. physiol. Chem.*, **247**, 185 (1937).

¹⁵⁷ Windaus, A., Lettré, H., and Schenck, F., *Annalen*, **520**, 98 (1935).

¹⁵⁸ Jendrassik, A., and Kemenyfi, A. G., *Biochem. Z.*, **189**, 180 (1927); **201**, 269 (1928).

¹⁵⁹ Bills, C. E., Honeywell, E. M., and MacNair, W. A., *J. Biol. Chem.*, **76**, 251 (1928).

¹⁶⁰ Kon, S. K., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 2573 (1928).

¹⁶¹ Koch, F. C., Koch, E. M., and Ragins, I. K., *J. Biol. Chem.*, **85**, 141 (1929).

¹⁶² Koch, F. C., Koch, E. M., and Lemon, H. B., *J. Biol. Chem.*, **85**, 159 (1929).

^{162a} Actually 7-dehydrocholesterol has a similar absorption spectrum.

¹⁶³ Yoder, L., *J. Biol. Chem.*, **116**, 71 (1936); Eck, J. C., Thomas, B. H., and Yoder, L., *Ibid.*, **117**, 655 (1937); Eck, J. C., and Thomas, B. H., *Ibid.*, **119**, 621 (1937).

¹⁶⁴ De Caro, M., *Boll. soc. ital. biol. sper.*, **7**, 1097 (1932); *Chem. Abs.*, **27**, 1035 (1933).

¹⁶⁵ Gustavson, R. G., *J. Colorado-Wyoming Acad. Sci.*, **1**, 23 (1929); *Chem. Abs.*, **26**, 3547 (1932).

¹⁶⁶ This work was reviewed by Holmes, A. D., *New England J. Med.*, **204**, 211 (1931); *Chem. Abs.*, **26**, 179 (1932).

¹⁶⁷ Hess, A. F., and Supplee, G. C., *Proc. Soc. Exptl. Biol. Med.*, **27**, 609 (1930).

1 per cent of cod-liver oil to their rations. A supplement of irradiated ergosterol equivalent in rat experiments to many times this amount of vitamin D failed, however, to afford protection. In experiments on White Leghorns, Massengale and Nussmeier¹⁶⁸ found it necessary to administer a quantity of irradiated ergosterol equivalent by rat assay to 200 per cent of cod-liver oil in order to produce the effects which could be produced by a 2-per cent (by rat assay) addition of cod-liver oil. Similar results were reported by Mussehl and Ackerson.¹⁶⁹ In the many subsequent confirmatory observations, which need not be discussed in detail, it was suggested by some that the presence of vitamin A in the cod-liver oil might by a synergistic action account for the greater effectiveness of the natural over the artificial vitamin.¹⁷⁰ This, however, was shown not to be the case by Russell and Klein,¹⁷¹ and the opinion that the vitamin of cod-liver oil is different from the artificial vitamin was shared by Bills.¹⁷² Thus there appeared to be two forms of the vitamin (but this number has since been increased). Amounts of the two that were equally effective for the rat were not equally effective for the chicken, far less of the natural than of the artificial vitamin being required for that species.¹⁷³

The human seems intermediate between the chick and the rat in its response. Hess, Lewis and Rivkin¹⁷⁴ found that about three rat units of an ergosterol preparation are clinically equivalent to one rat unit of cod-liver oil.¹⁷⁵ Drake,^{175a} however, has found no essential difference in their effects on infants.

PRODUCTS RELATED TO CHOLESTEROL AS PRECURSORS OF THE NATURAL D.

Waddell¹⁷⁶ as a result of extensive studies directed toward an explanation of the great effectiveness of direct irradiation of the chick in comparison with the effectiveness of irradiated ergosterol, suggested either that the course of the irradiation changes of ergosterol within the skin is different from that *in vitro* or that the precursor in the skin is not ergosterol. To decide this question, he irradiated crude cholesterol in order to study any products which might be formed in the skin by natural contaminants of cholesterol. It was found that the irradiated crude cholesterol gave better protection against leg weakness in chicks than did irradiated ergosterol, rat unit for rat unit. The idea that this might be ascribed to an improved absorption of ergosterol in the presence of

¹⁶⁸ Massengale, O. N., and Nussmeier, M., *J. Biol. Chem.*, **87**, 423 (1930).

¹⁶⁹ Mussehl, F. E., and Ackerson, C. W., *Poultry Sci.*, **9**, 334 (1930); *Chem. Abs.*, **26**, 2221 (1932).

¹⁷⁰ See, for example, Dalmer, O., von Werder, F., and Moll, T., *Z. physiol. Chem.*, **224**, 86 (1934).

¹⁷¹ Russell, W. C., and Klein, D., *Poultry Sci.*, **10**, 269 (1930); *Chem. Abs.*, **26**, 2222 (1932).

¹⁷² Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935). The vitamin from irradiated cholesterol seems as effective as that from cod-liver oil for laying birds. Bethke, R. M., Record, P. R., Wilder, O. H. M., and Kennard, D. C., *Poultry Sci.*, **16**, 438 (1937); *Chem. Abs.*, **32**, 980 (1938).

¹⁷³ Other papers relating to these species differences: Russell, W. C., Taylor, M. W., and Wilcox, D. E., *J. Biol. Chem.*, **107**, 736 (1934); Dols, M., *IV Congr. intern. tech. chim. ind. agr. Bruxelles*, **1**, IC (1935); *Chem. Abs.*, **30**, 5267 (1936); Supplee, G. C., Flanagan, G. E., Kahlenberg, O. J., and Hess, A. F., *J. Biol. Chem.*, **91**, 773 (1931); Steenbock, H., Kietzien, S., and Halpin, J. G., *Ibid.*, **97**, 249 (1932); Tully, W. C., Hauge, S. M., Carrick, C. W., and Roberts, R. E., *Poultry Sci.*, **10**, 310 (1931); Hunter, J. E., Dutcher, R. A., and Knandel, H. C., *Ibid.*, **11**, 239 (1932); Branion, H. D., and Smith, J. B., *Ibid.*, **11**, 261 (1932); *Chem. Abs.*, **27**, 1032 (1933); King, E. J., Hull, H., and Hall, G. E., *Poultry Sci.*, **12**, 129 (1933); *Chem. Abs.*, **27**, 3504 (1933); DeVaney, G. M., Munsell, H., and Titus, H. W., *Poultry Sci.*, **12**, 215 (1933); *Chem. Abs.*, **27**, 5380 (1933); Halvorson, H. A., and Lachat, L. L., *J. Assoc. Official Agr. Chem.*, **19**, 598, 628, 637, 647 (1936).

¹⁷⁴ Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, **94**, 1885 (1930); Hess, A. F., and Lewis, J. M., *Ibid.*, **99**, 647 (1932); **101**, 181 (1933). *Contra*, Bacharach, A. L., *Food*, **6**, 180 (1937); *Chem. Abs.*, **31**, 5415 (1937).

¹⁷⁵ See also Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, **39**, 45 (1930); Prather, E. O., Nelson, M., and Bliss, A. R., Jr., *Ibid.*, **42**, 52 (1931).

^{175a} Drake, T. G. H., *Am. J. Diseases of Children*, **53**, 754 (1937).

¹⁷⁶ Waddell, J., *J. Biol. Chem.*, **105**, 711 (1934).

large amounts of cholesterol was excluded by subsequent experiments. When the cholesterol had been purified by refluxing half an hour with hot ethanol containing potassium hydroxide followed by treatment with charcoal, similar good results were obtained. Repeated irradiations of cholesterol with removal of the activated product gradually exhausted the activatability of the cholesterol, indicating that it was not the cholesterol itself which was the provitamin. When ergosterol was irradiated in the presence of purified cholesterol the vitamin produced was no more effective than that resulting from the irradiation of the ergosterol alone. These experiments were important in indicating that there is in crude cholesterol a provitamin other than ergosterol which is capable of yielding a vitamin more potent to chicks than that obtainable from ergosterol.

In crude ergosterol no provitamin other than ergosterol itself could be detected by Bills, Massengale, McDonald and Wirick,¹⁷⁷ in analogous experiments.

Further evidence, now known to have been erroneous, also stimulated the investigation of the non-identity of the vitamin in cod liver oil with that of irradiated ergosterol. Rygh¹⁷⁸ concentrated the vitamin from cod liver oil about 20,000 times and concluded the active product to show no absorption maximum between 2600 and 2700 Å. Various other properties also differed from those of D₂, which led him to conclude them to be different substances. Ender¹⁷⁹ reached similar conclusions from ultraviolet absorption studies of a concentrate from tuna fish liver oil.

The provitamin of crude cholesterol is destroyed during a purification through the dibromide. The provitamin content of the purified material may then be increased by heat treatment, according to Hathaway and Lobb.¹⁸⁰ This confirmed an earlier observation of Hathaway and Koch¹⁸¹ who used a temperature of 200°C. At 300°C., however, the provitamin is materially destroyed within four hours. The provitamin was formed in the cholesterol fractions which were the most difficultly soluble in alcohol. There was no evidence of the formation of any ergosterol during the heat treatment and the vitamin produced on irradiation was in its effects on the chick more similar to the natural liver oil vitamin than that obtained by the irradiation of ergosterol. Absorption bands in the heated purified cholesterol were observed by Haman and Steenbock,¹⁸² who also showed that the provitamin is one which yield a vitamin similar to that of the fish oils. They also observed that irradiated plant oils were less effective for chicks than irradiated animal fats, thus aiding in focusing attention upon a derivative of cholesterol as the natural provitamin.

By use of adsorption methods applied to a sample of cholesterol as acetate which contained 4.5 per cent of the new provitamin, Boer, Reerink, Van Wijk and van Niekerk¹⁸³ succeeded in isolating the provitamin, first as acetate and after saponification, as the free sterol. It was possible to show its identity with 7-dehydrocholesterol, both by a comparison of the properties of the samples, and by their biological activity after irradiation. By the use of similar chromato-

¹⁷⁷ Bills, C. E., Massengale, O. N., and Wirick, A. M., *J. Biol. Chem.*, **108**, 323 (1935).

¹⁷⁸ Rygh, O., *Nature*, **136**, 396 (1935).

¹⁷⁹ Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); **3**, 161 (1934); *Chem. Abs.*, **28**, 4103, 7422 (1934).

¹⁸⁰ Hathaway, M. L., and Lobb, D. E., *J. Biol. Chem.*, **113**, 105 (1936).

¹⁸¹ Hathaway, M. L., and Koch, F. C., *J. Biol. Chem.*, **108**, 773 (1935).

¹⁸² Haman, R. W., and Steenbock, H., *J. Biol. Chem.*, **114**, 505 (1936); see also Roffo, A. H., Calgano, O., and Roffo, A. E., Jr., *Bull. Soc. Chim. Biol.*, **17**, 203 (1935).

¹⁸³ Boer, A. G., Reerink, E. H., van Wijk, A., and van Niekerk, J., *Proc. Acad. Sci. Amsterdam*, **39**, 622 (1936); *Chem. Abs.*, **30**, 5635 (1936).

graphic methods, Brockmann¹⁸⁴ isolated the natural vitamin from tuna fish liver oils and from halibut liver oil.¹⁸⁵

Windaus, Schenck and van Werder¹⁸⁶ showed that irradiation of 7-dehydrocholesterol in benzene with a magnesium spark gave a product of high antirachitic activity. Tachysterol-3 is first formed. The crude irradiation product was purified through the crystalline dinitrobenzoate and allophanate. These derivatives on saponification yielded the vitamin in the form of a non-crystallizing oil with an absorption maximum at 2650A, similar to that of D₂. The new material was called D₃. It was subsequently obtained in crystalline form by Schenck.¹⁸⁷ It melts at 82-4°C. and has $[\alpha]_D^{20} = +83.3^\circ$. It will be noted that 7-dehydrocholesterol has the same disposition of double bonds in the ring B as has ergosterol and the vitamin produced by irradiation differs from D₂ only in the side-chain, the double bond at positions 22 to 23 and the methyl group at carbon 24 of D₂ being lacking in D₃. As first prepared, the rat potency of D₃ appeared somewhat lower than that of D₂, 30×10^6 I.U. per gram as compared with 40×10^6 .¹⁸⁸ Subsequently, however, Brockmann and Busse¹⁸⁹ found D₃ crystals from tuna fish liver to have 40,000 I.U. per mg.

Irradiation of 7-dehydrocholesterol with wave-lengths longer than 2800A gives lumisterol-3 which probably differs from lumisterol only in the steric arrangement of groups at carbon atom 10.

The contaminant of cholesterol obtained from spinal cords was found to be 7-dehydrocholesterol or some similar derivative with two double bonds in ring B by Koch and Koch.¹⁹⁰ They believed, however, that the provitamin in heated cholesterol is some quite different material which does not have these double bonds. This material might be present in crude cholesterol, since it was possible to eliminate the impurity with the characteristic absorption spectrum from spinal cord cholesterol and still have a product so potent that, after irradiation, 0.1 to 3.0 mg. equals one rat unit. It was pointed out that the antirachitic potency which can be attained by a provitamin is conditioned not only by the two double bonds in ring B but also by the nature of the side-chain.

The provitamin of pig skin is 7-dehydrocholesterol according to Windaus and Bock,¹⁹¹ who isolated it as dinitrobenzoate. That of egg yolk sterols is ergosterol.¹⁹² It is possible that there is no ergosterol in skin, since its past identification had been based solely upon the absorption spectrum, which is similar to that of 7-dehydrocholesterol.

An analogous compound, 7-dehydrositosterol, prepared by Wunderlich,¹⁹³ was found capable of yielding an antirachitic substance on irradiation, but its potency was forty times less than that of D₂. The dehydrositosterol also undergoes the photosensitized conversion to a pinacol type of bimolecular compound.

¹⁸⁴ Brockmann, H., *Z. physiol. Chem.*, **241**, 104 (1936).

¹⁸⁵ Brockmann, H., *Z. physiol. Chem.*, **245**, 96 (1937). See also Haslewood, G., and Drummond, J. C., *Chemistry and Industry*, 598 (1936); Simonds, E., and Zucker, T., *J. Am. Chem. Soc.*, **58**, 2655 (1936); Neracher, O., and Reichstein, T., *Helv. Chim. Acta*, **19**, 1382 (1936). Two or more forms of vitamin may exist in fish oils, according to Bills, C. E., Massengale, O. N., Imboden, M., and Hall, H., *J. Nutrition*, **13**, 435 (1937); Hickman, K. C. D., and Gray, E. LeB., *Ind. Eng. Chem.*, **30**, 796 (1938).

¹⁸⁶ Windaus, A., Schenck, F., and von Werder, F., *Z. physiol. Chem.*, **241**, 100 (1936); Windaus, A., Deppe, M., and Wunderlich, W., *Annalen*, **533**, 118 (1937).

¹⁸⁷ Schenck, F., *Naturwiss.*, **25**, 159 (1937). D₃ is said to be twice as active as D₂ on infants by Brockmann, H., *Klin. Wochschr.*, **16**, 1383 (1937).

¹⁸⁸ Zucker, T. F., Simons, E. J., Colman, H. C., and Demarest, B., *Naturwiss.*, **26**, 11 (1938).

¹⁸⁹ Brockmann, H., and Busse, A., *Naturwiss.*, **26**, 122 (1938). See also Ramp, D. G., and Marshall, I. H., *J. Nutrition*, **15**, 525 (1938).

¹⁹⁰ Koch, E. M., and Koch, F. C., *J. Biol. Chem.*, **116**, 757 (1936).

¹⁹¹ Windaus, A., and Bock, F., *Z. physiol. Chem.*, **245**, 168 (1936).

¹⁹² Windaus, A., and Stange, O., *Z. physiol. Chem.*, **244**, 218 (1936).

¹⁹³ Wunderlich, W., *Z. physiol. Chem.*, **241**, 116 (1936).

Urushibara and Ando¹⁹⁴ described the photochemical dehydrogenation of an alcoholic solution of 7-dehydrocholesterol by sunlight in the presence of eosin. After a week there were obtained flocculent needles considered to be, in analogy with the behavior of ergosterol, 7-dehydrocholestenopinacone.

A search has been made for other provitamins. Weinhouse and Kharash¹⁹⁶ irradiated a series of tertiary alcohols or their dehydration products obtained by the action of various Grignard reagents on 7-ketocholesteryl acetate. The only one which showed slight antirachitic activity when irradiated was 7-isobutylidenecholesterol. Uraki¹⁹⁹ observed that irradiation of α -cholatrienic acid in chloroform for nine hours changed the specific rotation from -22.63° to $+2.4^\circ$. The product was a non-crystallizing resin which could be hydrogenated to cholanolic acid. The β -choladienic acid from desoxycholic acid was not altered by ultraviolet rays. It appeared that the point of attack in cholatrienic acid was the B ring, a shifting of the double bond occurring. Kikuzawa¹⁹⁷ reported the irradiated methyl α -cholate to have a slight antirachitic action. The β - derivative had less.

Rygh¹⁹⁸ recently found evidence for the occurrence in butter and ether extracts of hay and beef liver of an antirachitic substance which differed from other antirachitic vitamins in occurring to a larger extent in the saponifiable than in the unsaponifiable fraction. Kon and Booth¹⁹⁹ observed that the saponification of butter caused a loss of 80 per cent of its antirachitic potency.

The sterols from cacao-bean butter (theosterols) can be made antirachitic by irradiation.²⁰⁰

A recent review of the relative potencies for the rat and the chick of the antirachitic substances produced, chemically, by irradiation, or occurring in natural sources (particularly the fish liver oils of different species), has been given by Bills.²⁰¹ Grab²⁰² concluded the crystalline product from irradiated 7-dehydrocholesterol to be equivalent in its effects on the rat and the chick to a crystalline product isolated from tuna-liver oil. This material he called D₃. The difference of a methyl group between irradiated 7-dehydrocholesterol and irradiated 22-dihydroergosterol resulted in but little difference in physiological activity. Sterols with 29 carbon atoms are scarcely to be considered natural provitamins since the activities of 7-dehydrositosterol and 7-dehydrostigmastanol were very low. D₂ is somewhat less potent on the rat and considerably less potent on the chick than D₃.

Colorimetric methods are of limited use for the assay of vitamin D₂. These are based upon the spectrophotometric measurement of the intensity of an absorption band at 5000A produced by the addition of antimony trichloride or of one produced by aluminum chloride.²⁰³ A color test with sodium selenite is given

¹⁹⁴ Urushibara, Y., and Ando, T., *Bull. Chem. Soc. Japan*, **11**, 802 (1936); **12**, 495 (1937); *Chem. Abs.*, **31**, 2100 (1937). For similar work on 2,4-cholestadiene, see Skau, E. L., and Bergmann, W., *J. Am. Chem. Soc.*, **60**, 986 (1938); Butenandt, A., and Kudssus, H., *Z. physiol. Chem.*, **253**, 1, 224 (1938).

¹⁹⁶ Weinhouse, S., and Kharash, M. S., *J. Org. Chem.*, **1**, 490 (1936).

¹⁹⁸ Uraki, J., *Z. physiol. Chem.*, **221**, 40 (1933); *Chem. Abs.*, **28**, 168 (1934).

¹⁹⁷ Kikuzawa, T., *Z. physiol. Chem.*, **220**, 54 (1933); see also Okii, I., *J. Biochem. Japan*, **18**, 45 (1933); *Chem. Abs.*, **27**, 5425 (1933).

¹⁹⁹ Rygh, O., *Nature*, **133**, 533 (1934); *Z. Vitaminforschung*, **3**, 164 (1934); *Chem. Abs.*, **28**, 7315 (1934).

¹⁹⁹ Kon, S. K., and Booth, R. G., *Biochem. J.*, **27**, 1302 (1933); **28**, 111 (1934).

²⁰⁰ Labbe, H., de Balsac, F., and Lerat, R., *Bull. soc. therap.*, **35**, 71 (1930); *Chem. Abs.*, **24**, 982 (1930); **25**, 729 (1931); Knapp, A. W., and Coward, K. H., *Biochem. J.*, **29**, 2728, (1935).

²⁰¹ Bills, C. E., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 328 (1935); *J. Am. Med. Assoc.*, **108**, 13 (1937). Cf. also Hume, E. M., *Nutrition Abstracts and Reviews*, **6**, 891 (1937); von Wendt, G., *Voprosy Pitaniya*, **5**, No. 4, 31 (1936); *Chem. Abs.*, **31**, 2659 (1937).

²⁰² Grab, W., *Z. physiol. Chem.*, **243**, 63 (1936).

²⁰³ Brockmann, H., and Chen, Y. H., *Z. physiol. Chem.*, **241**, 129 (1936); Emmerie, A., and van Eekelen, M., *Acta Brevia, Neerland. Physiol., Pharmacol. Microbiol.*, **6**, No. 9-10, 133 (1936); *Chem. Abs.*, **31**, 1448 (1937); Halden, W., and Tzoni, H., *Nature*, **137**, 909 (1936); *Naturwiss.*, **24**, 296 (1936); Tzoni, H., *Biochem. Z.*, **287**, 18 (1936); Brückner, J., *Biochem. Z.*, **270**, 346 (1934); Wait, R., *Pharm. Zentralhalle*, **78**, 237 (1937).

by D₂ but not by cholesterol before or after irradiation.²⁰⁴ Biological assay methods, however, have been employed most frequently in the development of our knowledge of these substances. Their discussion, as well as that of the effects of the sterol irradiation products on the mineral metabolism, lies beyond the scope of this work.

Physiological Effects. In general, the administration of pure irradiation products leads to the effects on blood calcium and phosphorus and on bone calcification that result on general irradiation of the experimental animal. It would add but little to recount the many earlier experiments in which indefinite irradiation products, frequently contaminated with either inert or with predominantly toxic products, had been used.²⁰⁵

Robinson and Rosenheim²⁰⁶ found vitamin D to exert no demonstrable action on the calcification or decalcification of bone slices *in vitro*, but Venar and Todd²⁰⁷ report that the extent and density of mineralization of bone fragments from rachitic mice may be increased by the addition of small amounts of an aqueous emulsion of irradiated ergosterol to the calcifying medium in which the bones are immersed. Similar effects may be attained by the use of cod-liver oil or by irradiating the cultures by a sunlamp.²⁰⁸

Harris²⁰⁹ believes the vitamin to function by increasing the net absorption of calcium and phosphates from the intestine, thus tending to raise the level of the blood calcium or phosphate. The latter rise automatically brings about increased calcification in sites provided with the bone-calcifying enzyme, phosphatase. Hottinger²¹⁰ suggested that it renders innocuous some inhibitor of calcium assimilation, possibly an enzyme capable of decomposing glycerophosphates or hexosephosphates. Taylor and Weld²¹¹ were of the opinion that, at least in young dogs, there is no evidence that irradiated ergosterol increases calcium absorption; indeed they state that even small doses increase the excretion of calcium.

One speculation as to the mechanism by which the vitamin functions regards it as liberating inorganic phosphorus from the lipins of the body, a deficiency of inorganic phosphate being regarded as the essential cause of rickets.²¹² Nicolaysen²¹³ finds that in rachitic rats, inorganic phosphorus is reduced in the muscles, liver and kidneys. Massive doses of the vitamin increased it to normal, but therapeutic doses caused only a slight increase of the inorganic phosphorus of the kidney.²¹⁴ In D deficient rats, the percentage of inorganic phosphorus in the red blood cells is reduced, but that of easily hydrolyzable phosphoric esters is increased.²¹⁵ Warkany²¹⁶ observed that rabbits which usually excrete no phosphates, eliminate large quantities in the urine within 48 hours after the administration of 30 to 100 mg. of irradiated ergosterol in their food.

In artificial cultures of the skeletal tissues of the embryo chick, phosphatase

²⁰⁴ Levine, V. E., and McKay, F. M., *Proc. Soc. Exp. Biol. Med.*, **33**, 546 (1936).

²⁰⁵ See Laurens, H., "The Physiological Effects of Radiations," New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1933. For more recent studies, Crimm, P. D., Strayer, J. W., Watson, H. L., and Heimann, G., *Am. Rev. Tuberc.*, **28**, 202 (1933); *Chem. Abs.*, **28**, 806 (1934); Morgan, A. F., Garrison, E. A., Householder, H., Hansen, A. M., Seberger, M. V., Watenpaugh, J. T., Felsner, A., and Long, N. L., *Univ. California Pub. Physiol.*, **8**, 61 (1934); *Chem. Abs.*, **28**, 7315 (1934); Freeman, S., *Am. J. Physiol.*, **115**, 701 (1936); Johnson, R. M., *J. Clin. Investigation*, **16**, 223 (1937).

²⁰⁶ Robinson, R., and Rosenheim, A. II., *Biochem. J.*, **28**, 684 (1934).

²⁰⁷ Venar, Y., and Todd, T. W., *J. Lab. Clin. Med.*, **22**, 221 (1936); see also Dejust, L. H., *Rev. actinologie physiotherap.*, **6**, 1 (1931); *Chem. Abs.*, **26**, 2792 (1932).

²⁰⁸ Yoshitomi, M., *J. Biochem. Japan*, **21**, 37 (1935); *Chem. Abs.*, **29**, 2590 (1935).

²⁰⁹ Harris, L., *Lancet*, **I**, 1031 (1932); *Chem. Abs.*, **27**, 2187 (1933).

²¹⁰ Hottinger, A., *Naturwiss.*, **16**, 484 (1928).

²¹¹ Taylor, N. B., and Weld, C. B., *Trans. Roy. Soc. Canada*, **26**, 9 (1932); *Chem. Abs.*, **27**, 1922 (1933).

²¹² McGowan, J. P., Cunningham, I. J., and Auchinachie, D. W., *Biochem. J.*, **25**, 1295 (1931); McGowan, J. P., *Ibid.*, **27**, 943 (1933).

²¹³ Nicolaysen, R., *Biochem. J.*, **30**, 1329 (1936); see also *Biochem. J.*, **31**, 101, 105, 107, 122, 328 (1937).

²¹⁴ See also Jones, J. H., and Cohn, B. N. E., *J. Nutrition*, **11**, 293 (1936); Duffau, R., [*Compt. rend. soc. biol.*, **124**, 1194 (1937)] finds an increase of about 10% in the orthophosphates of muscles in rickets.

²¹⁵ Von Euler, H., and Brandt, K., *Z. physiol. Chem.*, **240**, 215 (1936).

²¹⁶ Warkany, J., *Klin. Wochschr.*, **9**, 2152 (1930); *Chem. Abs.*, **25**, 1877 (1931).

appears early.²¹⁷ Heymann²¹⁸ found that under the influence of irradiated ergosterol, phosphatase activity *in vitro* is unchanged, but ultraviolet irradiation caused inhibition of the enzyme in about 40 per cent of the tests. The enzyme is greatly increased in chicks with rickets.²¹⁹ In laying hens there is a high range of variation of the serum phosphatase which is not reduced by the administration of irradiated ergosterol. Plasma phosphatase is increased in rachitic children less than two years of age. Its continued rise may be prevented by the use of vitamin D.²²⁰

Morelle²²¹ studied the healing of experimental fractures in three groups of rats receiving respectively 1, 10, and 2 to 4 mg. of irradiated ergosterol per day. No effects were apparent before the twentieth day, but after that time the fracture lines were invisible in those receiving the medium dose, although they were still apparent in controls. After the thirtieth day, there was a dense callus in the treated animals and in the controls the disappearance of the fracture line had just begun. Heavy doses caused abnormally dense and exuberant callus formation. The conclusion of Grauer²²² from similar experiments was that therapeutic doses stimulate the osteogenic layer and favor repair. Overdoses stimulate the fibrous layer of the periosteum by decalcification of bones and retard repair. Fischer and Key,²²³ however, are of the opinion that the addition of either calcium or vitamin D to the diet does not lessen the local atrophy of disuse or accelerate the union of bones.

Although some have expressed the view that the vitamin acts by stimulating the parathyroids, this is by no means generally conceded.²²⁴ Comel²²⁵ believed that after removal of the parathyroids life could be maintained indefinitely by giving vitamin D, but Lesné, Dubois and Simonnet²²⁶ find that it does not serve as a substitute for the hormone.²²⁷

Dosage. As early as 1927, reports of the clinical efficacy of irradiated ergosterol began to appear.²²⁸ The use of a preparation of irradiated ergosterol as a comparison standard for the assay of the antirachitic action was described by Coward and adopted by the British Pharmaceutical Society.²²⁹ Its potency was such that a daily dose of not more than 0.1 γ produced complete healing of rickets induced in rats under prescribed conditions. The unit of antirachitic potency was then defined as the amount of activity contained in 0.1 γ of the standard preparation. The standard subsequently adopted by the Medical Research Council was prepared by freeing the irradiation product from alcohol, and dissolving it in pure unadulterated olive oil, the volume being adjusted to make a known concentra-

²¹⁷ Croxatio, H., *Compt. rend. soc. biol.*, 108, 117 (1931); *Chem. Abs.*, 26, 3009 (1932); see also Fischmann, C. F., *Arch. exptl. Zellforsch.*, 19, 211 (1937); *Chem. Abs.*, 31, 8618 (1937).

²¹⁸ Heymann, W., *Biochem. Z.*, 227, 1 (1930); see also Bauer, W., Marble, A., and Clafin, D., *J. Clin. Investigation*, 11, 21, 37, 47 (1932).

²¹⁹ Common, R. H., *J. Agr. Sci.*, 26, 492 (1936); *Chem. Abs.*, 30, 8327 (1936).

²²⁰ Stearns, G., and Warweg, E., *Am. J. Diseases of Children*, 49, 79 (1935); *Chem. Abs.*, 29, 2581 (1935); Morris, N., Stevenson, M. M., Peden, O. D., and Small, J., *Arch. Diseases of Childhood*, 12, 45 (1937). Compare earlier negative findings of Fabisch, W., *Biochem. Z.*, 254, 158 (1932); *Chem. Abs.*, 27, 525 (1933) and Rossi, A., and De Rienzo, A., *Boll. soc. ital. biol. sper.*, 8, 719 (1933); *Chem. Abs.*, 29, 2557 (1935).

²²¹ Morelle, J., *Rev. Belge Sci.*, 2, 226 (1930); *Chem. Abs.*, 25, 2463 (1931).

²²² Grauer, R. C., *Arch. Surgery*, 25, 1035 (1932); *Chem. Abs.*, 27, 1946 (1933).

²²³ Fischer, F., and Key, J. A., *Archiv. Surgery*, 29, 3112 (1934); *Chem. Abs.*, 28, 6796 (1934).

²²⁴ Thomson, D. L., and Collip, J. B., *Physiol. Rev.*, 12, 309 (1932).

²²⁵ Comel, M., *Arch. Fisiol.*, 29, 123 (1930); *Chem. Abs.*, 26, 180 (1932).

²²⁶ Leané, E., Dubois, R., and Simonnet, H., *J. Physiol. Path. Gén.*, 30, 65 (1932); *Chem. Abs.*, 26, 4876 (1932).

²²⁷ See also Popoviciu, G., and Nitescu, I. I., *Z. ges. Exptl. Med.*, 81, 656 (1932); *Chem. Abs.*, 27, 4565 (1933); Asher, D. W., and Jones, J. H., *J. Biol. Chem.*, 100, 333 (1933); Stacey, R. S., *Lancet*, II, 656 (1935); Deutsch, H., Reed, C. I., and Struck, H. C., *Am. J. Physiol.*, 117, 1 (1936); Brougher, J. C., *Ibid.*, 86, 538 (1928); Morgan, A. F., and Garrison, E. A., *J. Biol. Chem.*, 85, 687 (1930); Mathieu, F., *Compt. rend. soc. biol.*, 114, 1375 (1933); *Chem. Abs.*, 28, 1744 (1933); Dale, H. H., Marble, A., and Marks, H. P., *Proc. Roy. Soc.*, 111B, 522 (1932).

²²⁸ Hess, A. F., *J. Am. Med. Assoc.*, 89, 337 (1927); Schippers, J. C., *Nederland. Tijdschr. Geneesk.*, 72, 3898 (1928); *Chem. Abs.*, 22, 4154 (1928); Sobel, J., and Claman, I., *Arch. Ped.*, 46, 1 (1929); *Chem. Abs.*, 23, 1938 (1929).

²²⁹ Coward, K. H., *Quart. J. Pharm.*, 1, 27 (1928); *Chem. Abs.*, 22, 4154 (1928); *Lancet*, II, 503 (1930).

tion in terms of the ergosterol used. Such solutions retained their activity unchanged for two years if maintained at or below 0°C.

In practice, cod-liver oil was checked against this standard and adjusted to contain a definite concentration of the vitamin in terms of the standard. Unfortunately, much confusion arose in regard to the strength of the cod-liver oil adopted as comparison standard. The system of the British Medical Research Council called for a cod-liver oil containing 100 units per cc. This was altered by the League of Nations to 100 units per gram, the strength adopted in the U. S. Pharmacopoeia in 1934. The Steenbock system used an oil standardized to contain 37 units per gram and the Holmes system (employed for a time by the American Drug Manufacturers Association) one with 350 units per gram. Still other systems have been used in other countries.²³⁰

The present vitamin D unit²³¹ is equivalent to 0.025 γ of calciferol.

Bills²³² considers that the smallest dose which can be relied on to prevent rickets or to heal mild rickets in infants is about 3000 international units (I.U.) per day in the form of irradiated ergosterol or 1000 I.U. in the form of cod-liver oil. The Council on Pharmacy and Chemistry of the American Medical Association²³³ adopted the name Viosterol to designate irradiated ergosterol and Viosterol in Oil to designate a preparation containing the substance dissolved in oil. The qualifying phrases 100 D, 5 D, etc. were added to the label to indicate the potency as a multiple of the potency of good cod-liver oil.

The successful use of large doses, 10 to 20 drops daily of viosterol, in late rickets was described by Shelling and Hopper.²³⁴ Spence²³⁵ found calciferol as effective as cod-liver oil or irradiated ergosterol in human rickets. One cc. of a solution containing 3000 units, administered daily, produced a maximum curative effect.

Recently, there has been much discussion as to the effects of variations in the calcium and phosphorus of the diet given during the administration of the vitamin, but this cannot be considered here.²³⁶

Toxic Effects. Hypervitaminosis D. About 1928, it became evident that irradiated ergosterol preparations may exert toxic effects.²³⁷ Particularly dangerous properties were ascribed to the imported Vigantol.²³⁸ After the administration of large quantities of this material to rats, Herzenberg²³⁹ observed a necrosis in the smooth and striated muscles, followed by a deposition of calcium in the necrotic areas. The deposition of calcium was observed in the heart muscle and in elastic muscle fibers of blood vessel walls but the changes were different in character from those of arteriosclerosis. Schoenholz²⁴⁰ found that pregnant rats which had received an overdose (10 mg. of Vigantol per day), lost their appetites and became sick. The fetuses were resorbed *in utero* or aborted. The live young were very small and usually died. Calcium deposits were observed

²³⁰ See Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).

²³¹ *Quart. Bull. Health Org. League of Nations*, **3**, 428 (1934).

²³² Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).

²³³ *J. Am. Med. Assoc.*, **93**, 693 (1929).

²³⁴ Shelling, D. H., and Hopper, K. B., *Am. J. Diseases of Children*, **47**, 61 (1934).

²³⁵ Spence, J. C., *Lancet*, **225**, 911 (1933); *Chem. Abs.*, **28**, 5503 (1934).

²³⁶ See Bruce, H. M., and Callow, R. K., *Biochem. J.*, **28**, 512 (1934).

²³⁷ Wurzing, S., *Klin. Wochschr.*, **7**, 1859 (1928); *Chem. Abs.*, **24**, 3042 (1930); Reyher, P., and Walkoff, E., *Munch. Med. Wochschr.*, **75**, 1071 (1928); *Chem. Abs.*, **23**, 4728 (1929); Kreitmair, H., *Munch. Med. Wochschr.*, **75**, 637 (1928); Lusch, F., *Klin. Wochschr.*, **7**, 2148 (1928).

²³⁸ Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **91**, 783 (1928).

²³⁹ Herzenberg, H., *Beitr. Path. Anat.*, **82**, 27 (1929); *Chem. Abs.*, **23**, 4725 (1929); (Sclerosis in Man), Gerlach, W., *Munch. Med. Wochschr.*, **83**, 49 (1936).

²⁴⁰ Schoenholz, L., *Klin. Wochschr.*, **8**, 1257 (1929); *Chem. Abs.*, **24**, 890 (1930).

in the livers of some of the mothers. A number of German workers observed involvement of the kidneys. These observations stimulated a great number of publications, of which but a few need be cited.²⁴¹

A toxic calcification factor was defined²⁴² as the smallest amount which, given daily for a period of ten days, causes a mouse to lose 2.5 gm. in weight or to die. Mice receiving larger doses showed calcareous deposits in the kidneys. The ratio between the antirachitic rat dose and the mouse calcification factor was considered the therapeutic index of an irradiated ergosterol preparation.

It soon became evident that there were considerable differences between the antirachitic and toxic doses of variously irradiated preparations. With Vigantol, the margin of safety was very narrow.²⁴³ The spectrographic study of the irradiation process soon made it apparent why this was the case. It was prepared according to a patent²⁴⁴ which directed that the irradiation be continued until spectrographic observations indicated that there had been a maximum formation of a substance absorbing chiefly at 2480A. This is, as has been stated in a preceding section, now known to be toxisterol or substance 248, the over-irradiation product. Subsequently it has been learned that D₂ and even the D₃ of cod-liver oil are also toxic in large doses. It is, however, evident that the formation of substance 248 should be avoided, since it is not only toxic but its formation occurs at the expense of that of the true antirachitic substance. The toxicity of calciferol in large doses was demonstrated by Askew, Bourdillon, Bruce, Callow, Philpot and Webster and by other research groups.²⁴⁵

At one time, Holtz and Schreiber²⁴⁶ believed that the true vitamin when isolated would prove nontoxic and attempts were made to employ partition between immiscible solvents and various chemical procedures for separating the assumed toxic and antirachitic fractions. The failure of these attempts and the observation that D₁ had toxic properties led Windaus, Busse and Weidlich²⁴⁷ to agree that the true vitamin possesses toxicity. It was found possible by chemical means to destroy the antirachitic activity without lessening the toxicity, but the converse was not possible. The English workers found that the ratio of the toxic dose in mice to the curative dose in rats is about 4000 to 1. The finding that D₂ has toxic properties proved²⁴⁸ that Reiter had been in error in claiming that irradiation with wave-lengths longer than 2800A produces a non-toxic product.²⁴⁹ It is, of course, true that the use of such long wave-lengths lessens the danger of the production of the toxic substance 248 by overirradiation. Whether or not tachysterol itself has toxic properties is not yet known, but its thermal decomposition products are highly toxic.²⁵⁰

²⁴¹ Bamberger and Spranger, *Deut. Med. Wochschr.*, **54**, 1116 (1928); Wiskott, A., *Munch. Med. Wochschr.*, **75**, 1445 (1928); Adam, A., *Klin. Wochschr.*, **7**, 1825 (1928); Degkwitz, R., *Munch. Med. Wochschr.*, **75**, 1631 (1928); Bamberger, Ph., *Deut. Med. Wochschr.*, **55**, 399 (1929); György, P., *Klin. Wochschr.*, **8**, 684 (1929); Putschar, W., *Z. Kinderheilk.*, **48**, 269 (1929); Klausner-Cronheim, I., *Deut. Med. Wochschr.*, **56**, 1566 (1930).

²⁴² Holtz, F., Lacquer, F., Kreitmair, H., and Moll, T., *Biochem. Z.*, **237**, 247 (1931); *Munch. Med. Wochschr.*, **78**, 1688 (1931); *Chem. Abs.*, **26**, 3011 (1932).

²⁴³ Göttsche, O., and Kellner, B., *Arch. Kinderheilk.*, **94**, 129 (1931).

²⁴⁴ British P. 296,093, Nov. 15, 1928, to I. G. Farbenind. A.-G.

²⁴⁵ Askew, F. A., Bourdillon, R. B., Bruce, H. M., Callow, R. K., Philpot, J., and Webster, T. A., *Proc. Roy. Soc.*, **109**, 488 (1932); Dale, H. H., Maible, A., and Marks, H. P., *Ibid.*, **111B**, 522 (1932); Gough, J., Duguid, J. B., and Davies, D. R., *Brit. J. Exptl. Path.*, **14**, 137 (1933); Harris, L. J., and Moore, T., *Biochem. J.*, **22**, 1461 (1928); Harris, L. J., and Innes, J., *Ibid.*, **25**, 367 (1931).

²⁴⁶ Holtz, F., and Schreiber, E., *Z. physiol. Chem.*, **191**, 3 (1930); Windaus, A., and Aubagen, E., *Z. physiol. Chem.*, **196**, 108 (1930); **197**, 167 (1931).

²⁴⁷ Windaus, A., Busse, P., and Weidlich, G., *Z. physiol. Chem.*, **202**, 246 (1931).

²⁴⁸ Lacquer, F., *Klin. Woch.*, **10**, 1072 (1931); *Deut. Med. Wochschr.*, **57**, 243 (1931); *Chem. Abs.*, **26**, 3010 (1932).

²⁴⁹ Reiter, T., *Naturwiss.*, **17**, 876 (1929); Kisch, E., and Reiter, T., *Deut. med. Wochschr.*, **56**, 2034 (1930); *Chem. Abs.*, **25**, 4918 (1931).

²⁵⁰ Windaus, A., and Lüttringhaus, A., *Deut. Med. Wochschr.*, **58**, 1669 (1932).

A review of the nature of the toxic effects of D_2 and of cod-liver oil has been given by Agduhr, Blix and Vahlquist.²⁵¹ A fatal case in a child has been described by Thatcher.²⁵² Ham and Lewis²⁵³ found that large doses of vitamin D given to normal young rats interfered with the processes of bone calcification and actually produced rachitic lesions. They suggested that the action may be to increase the attraction of the blood for calcium. Baumgartner, King and Page²⁵⁴ found overdoses to produce softening of the skeletal framework of rabbits and a low bone phosphatase. The ratio of calcium to phosphorus in the bone is not affected according to Kramer, Shear and McKenzie.²⁵⁵

That the hypercalcemia alone is not responsible for the toxic effects, since it is compatible with life, is the belief of Taylor, Weld and Sykes.²⁵⁶

It is generally found that the hypercalcemia may be produced even on a low calcium diet, some claiming at the expense of the bones.²⁵⁷

Daily subcutaneous injections of irradiated ergosterol produce local calcification in the subcutaneous tissues, according to von Brand and Holtz. Calcification in the kidneys is less than after the oral administration of the same doses.²⁵⁸ In general, after a toxic state with calcium deposition has been reached, the discontinuance of the administration of the vitamin leads to a reversal of the process and the repair of the lesions.²⁵⁹ Both human subjects and dogs usually survive 20,000 to 30,000 units per kg. per day for indefinite periods. In rats, it is agreed by many that 10,000 times the minimum antirachitic dose is not lethal and several say not harmful.²⁶⁰ Bills and Wirick²⁶¹ found 1000 times overdosage to be just perceptibly harmful, 4000 times overdosage to be definitely injurious and 40,000 times overdosage strongly toxic. Harris and Moore²⁶² found a 100,000 times overdosage rapidly fatal, and Collazo, Rubino and Varela Fuentes²⁶³ found 50,000 times the normal dose fatal within six weeks. Young rats and puppies remained normal with doses up to 1000 times the minimal effective dose according to Cartland, Speer and Heyl.²⁶⁴

²⁵¹ Agduhr, E., Blix, G., and Vahlquist, B., *Uppsala Läkareföreningen*, 39, 304; 40, 183; *Chem. Abs.*, 29, 8145 (1935); for the pathologic anatomy, Duguid, J. B., *Lancet*, II, 983 (1930); Barr, D. P., *Physiol. Rev.*, 12, 593 (1932); Nitescu, I. I., and Bratiano, S., *Compt. rend. soc. biol.*, 121, 1533 (1936).

²⁵² Thatcher, L., *Edinburgh Med. J.*, 38, 457 (1931); *Chem. Abs.*, 25, 5446 (1931).

²⁵³ Ham, A. W., and Lewis, M. D., *Brit. J. Exptl. Path.*, 15, 228 (1934); *Chem. Abs.*, 28, 7301 (1934).

²⁵⁴ Baumgartner, L., King, E. J., and Page, I. H., *Biochem. Z.*, 213, 170 (1929); *Chem. Abs.*, 24, 403 (1930).

²⁵⁵ Kramer, B., Shear, M., and McKenzie, M. R., *J. Biol. Chem.*, 82, 555 (1929).

²⁵⁶ Taylor, N. B., Weld, C. B., and Sykes, J. F., *Brit. J. Exptl. Path.*, 17, 104 (1936). For the effects of small doses of concentrated preparations on the blood calcium and phosphorus of monkeys, see Cowdry, E. V., and Scott, G. H., *Arch. Path.*, 22, 1 (1936).

²⁵⁷ Soeur, R., *Arch. Int. Med. Exptl.*, 6, 365 (1931); *Chem. Abs.*, 25, 4588 (1931); Jones, J. H., and Rapoport, M., *J. Biol. Chem.*, 93, 153 (1931); Jones, J. H., and Robson, G. M., *Ibid.*, 91, 43 (1931); Thoenes, F., *Jahrbuch Kinderheilk.*, 126, 348 (1929); *Chem. Abs.*, 26, 501 (1932); *Jahrb. Kinderheilk.*, 129, 171 (1930); Jones, J. H., Rapoport, M., and Hodes, H. L., *J. Biol. Chem.*, 89, 647 (1930); Wiskott, A., *Z. Kinderheilk.*, 49, 79 (1930); *Chem. Abs.*, 26, 4362 (1932); Kern, R., Montgomery, M. E., and Still, E. U., *J. Biol. Chem.*, 93, 365 (1931); Cole, V. V., and Koch, F. C., *Ibid.*, 94, 263 (1931); Hess, A. F., Benjamin, H., and Gross, J., *Ibid.*, 94, 1 (1931); Pozzi, L., and Preto, E., *Biochem. therap. sper.*, 18, 397 (1932); *Chem. Abs.*, 27, 1667 (1933); Kletzien, S. W. F., Templin, V. M., Steenbock, H., and Thomas, B. H., *J. Biol. Chem.*, 97, 265 (1932); von Euler, H., and Rydholm, M., *Biochem. Z.*, 249, 141 (1932); Popoviciu, G., *Jahrb. Kinderheilk.*, 132, 286 (1931); *Chem. Abs.*, 26, 3013 (1932).

²⁵⁸ von Brand, T., and Holtz, F., *Z. physiol. Chem.*, 195, 241 (1931).

²⁵⁹ Steck, I. E., Deutsch, H., Reed, C. I., and Struck, H. D., *Ann. Internal Med.*, 10, 951 (1937); von Brand, T., and Holtz, F., *Z. physiol. Chem.*, 185, 217 (1929); for storage after massive doses, see Heymann, W., *J. Biol. Chem.*, 118, 371 (1937).

²⁶⁰ Rosenheim, O., and Webster, T. A., *Biochem. J.*, 21, 389 (1927); Light, R. F., Miller, G. E., and Frey, C. N., *J. Biol. Chem.*, 84, 487 (1929).

²⁶¹ Bills, C. E., and Wirick, A. M., *J. Biol. Chem.*, 86, 117 (1930).

²⁶² Harris, L. J., and Moore, T., *Biochem. J.*, 22, 1461 (1928).

²⁶³ Collazo, J. A., Rubino, P., and Varela Fuentes, B., *Biochem. Z.*, 204, 347 (1929).

²⁶⁴ Cartland, G. F., Speer, J. H., and Heyl, F. W., *J. Pharmacol.*, 36, 619 (1929); *Chem. Abs.*, 24, 404 (1930).

In the human, no ill effects were noted with 20 to 50 times the ordinary doses by Hess, Poncher, Dale and Klein,²⁶⁵ other than a tendency to constipation and colic. In patients with tetany no toxic effects were noted with 300 times overdosage.²⁶⁶ Bills believes that in man toxic effects begin to appear at 200 times the ordinary dose, that is when 600,000 I.U. of properly irradiated ergosterol are given daily over several weeks. Rappaport and Reed gave 3 cc. per day of a concentrated solution 10,000 D, and known to contain a million I.U. per gram. Although this was 2,760,000 I.U. or 920 times the ordinary therapeutic dose, no serious poisoning was produced. The largest recorded human dose, 6000 times the ordinary dose, produced hypercalcemia, but no pathological calcification of tissues.²⁶⁷

Excessive doses of fish-liver oils are less apt to produce hypervitaminosis.²⁶⁸

Relation to Tuberculosis. Because of the remedial effects of ultraviolet irradiation of tuberculous patients, many studies have been made of the effects of vitamin D in that disease in order to determine whether its action may account for the effects of general irradiation. The calcifying action of the vitamin might be expected to be of value in the treatment of the disease.²⁶⁹ Simonnet and Tanret²⁷⁰ found large doses of irradiated ergosterol to cause a notable increase in pulmonary calcification in tuberculous rabbits. In chronic tuberculosis the evolution of tubercles was checked. Pfannstiel and Scharlau²⁷¹ reported somewhat less favorable results on rabbits primarily infected but found favorable results in somewhat immunized rabbits. Meersseman and Tricault²⁷² found tuberculous guinea pigs given vitamin D to live longer and have less severe lesions than the controls. They also reported improvement in eleven human patients. Spies and Berryhill²⁷³ suggested a diet high in vitamin D for patients with intraperitoneal tuberculosis. Long²⁷⁴ agreed that viosterol by mouth increases calcification in experimental tuberculosis.

Many of those who obtained negative results did not employ massive doses.²⁷⁵ Haubold²⁷⁶ even claimed that small doses stimulated the disease in guinea pigs. Spies and Walker²⁷⁷ obtained less distinct results in experimental avian than in the bovine tuberculosis. Poncher and Gasul²⁷⁸ drew no conclusions as to the effect of moderately large doses in tuberculous children, but believed the secondary effects of such therapy unfavorable. Negative results in intestinal

²⁶⁵ Hess, J. H., Poncher, H. G., Dale, M. L., and Klein, R. I., *J. Am. Med. Assoc.*, **95**, 316 (1930).
²⁶⁶ Reed, C. I., and Seed, L., *Endocrinology*, **17**, 136 (1933); but see Rappaport, B. Z., and Reed, C. I., *J. Am. Med. Assoc.*, **101**, 105 (1933).

²⁶⁷ Spies, T. D., and Hanzal, R. F., *Proc. Soc. Exptl. Biol. Med.*, **31**, 747 (1935).

²⁶⁸ Morgan, A. F., Kimmel, L., and Hawkins, N. C., *J. Biol. Chem.*, **120**, 85 (1937); Martinelli, A., *Probl. alimentare*, **4**, 1 (1934); *Rev. ges. Physiol. exptl. Pharmacol.*, **87**, 82; *Chem. Abs.*, **31**, 7951 (1937).

²⁶⁹ The subject has been reviewed by Guilbert, G. D., *Mcd. Bull. Veterans' Admin.*, **10**, 141 (1934). See also Kaminsky, J., and Davidson, D., *Am. Rev. Tuberc.*, **22**, 48 (1930); Hildebrand, C. J., *Ibid.*, **22**, 53 (1930).

²⁷⁰ Simonnet, H., and Tanret, G., *Compt. rend.*, **190**, 1526 (1930).

²⁷¹ Pfannstiel, W., and Scharlau, B., *Beitr. klin. Tuberk.*, **73**, 351 (1930); *Chem. Abs.*, **25**, 2172 (1931).

²⁷² Meersseman, F., and Tricault, G., *Semana Med. Buenos Aires*, **1**, 595 (1931); *Chem. Abs.*, **25**, 2485 (1931).

²⁷³ Spies, T., and Berryhill, W. R., *Am. Rev. Tuberc.*, **26**, 275 (1932); *Chem. Abs.*, **27**, 775 (1933).

²⁷⁴ Long, E. R., *Proc. Soc. Exptl. Biol. Med.*, **30**, 1090 (1933).

²⁷⁵ Simonnet, H., and Tanret, G., *Presse Med.*, **39**, 932 (1931); Glayzel, H. G., Shear, M. J., and Kramer, B., *Am. Rev. Tuberc.*, **24**, 106 (1931); Kaminsky, J., and Davidson, D. L., *Ibid.*, **24**, 483 (1931); Freund, R., *Beitr. klin. Tuberk.*, **78**, 666 (1931); *Chem. Abs.*, **26**, 6012 (1932); Zeyland, J., and Piasecka-Zeyland, E., *Tubercle*, **17**, 198 (1936); Crimm, P. D., and Strayer, J. W., *Ann. Int. Med.*, **9**, 1393 (1936); Loewen, D. F., and Oatway, W. H., *J. Am. Rev. Tuberc.*, **33**, 733 (1936).

²⁷⁶ Haubold, H., *Z. Tuberk.*, **67**, 247 (1933); *Chem. Abs.*, **27**, 5100 (1933).

²⁷⁷ Spies, T., and Walker, T. T., *Am. Rev. Tuberc.*, **64**, 23, 65 (1931); **74**, 723 (1931).

²⁷⁸ Poncher, H. G., and Gasul, B. M., *Am. Rev. Tuberc.*, **30**, 358 (1934); *Chem. Abs.*, **28**, 7303 (1934).

tuberculosis have been reported by Steinbach and Rosenblatt.²⁷⁹ More or less favorable evidence for the use of irradiated ergosterol in tuberculosis is also to be found in the following papers.²⁸⁰

DeJust²⁸¹ reported the cure of two cases of tuberculous osteitis with fistulas after a score of instillations of viosterol into the fistulas.

Other Effects. Mellanby²⁸² called attention to the fact that exposure of puppies on a moderately defective diet to the rays of a mercury arc had a beneficial effect upon the calcification and structure of the teeth. If the diets were very bad, however, the calcification became poorer on irradiation. Later, Mellanby and Pattison²⁸³ found a cereal-free diet rich in calcium and vitamin D to almost eliminate the initiation and spread of caries in children. Similar favorable reports are due to Agnew, Agnew and Tisdall²⁸⁴ and others.²⁸⁵ Little evidence for a protective action of the vitamin against caries could be found, however, by Rosebury and Karshan²⁸⁶ or Shelling and Anderson.²⁸⁷ Blackberg and Berke²⁸⁸ noted a relationship in dogs between a deficiency in the vitamin and certain changes in the pulp, enamel and dentine which are poorly calcified.²⁸⁹

The use of irradiation in the treatment of hay fever and asthma finds some confirmation in the work of Rappaport, Reed, Hathaway and Struck,²⁹⁰ who observed that Viosterol, in large doses, combined with pollen injections is more effective than either alone. Rappaport and Reed²⁹¹ found Viosterol without effect in three cases of infectious asthma and two of urticaria, but it did protect six hay fever patients. Favorable effects of vitamin D on eczema have been reported.²⁹²

The ability of ergosterol to sensitize the pneumococcus to lysis by saponin is destroyed by irradiation.²⁹³

Viosterol has neither antiseptic nor bactericidal properties.²⁹⁴ Greene²⁹⁵

²⁷⁹ Steinbach, M. M., and Rosenblatt, M. B., *Am. Rev. Tuberc.*, **31**, 35 (1935), (*Chem. Abs.*, **29**, 4410 (1935)).

²⁸⁰ Levaditi, C., and Li, Y. P., *Compt. rend. soc. biol.*, **106**, 169 (1931), (*Chem. Abs.*, **25**, 3382 (1931)). Poliard, A., Ravault, P., and Barial, P., *Compt. rend. soc. biol.*, **104**, 633 (1930); (*Chem. Abs.*, **25**, 4916 (1931)); Pachioli, R., and Mengoli, V., *Bol. Soc. Ital. Biol. Sper.*, **6**, 448 (1931), (*Chem. Abs.*, **26**, 764 (1932)); Haubold, H., *Beitr. Path. Anat.*, **89**, 633 (1932), (*Chem. Abs.*, **26**, 5660 (1932)). Loewy, A., and Grüniger, W. Z., *Tuberk.*, **61**, 317 (1931); (*Chem. Abs.*, **26**, 6011 (1932); Crimm, P. D., *Am. Rev. Tuberc.*, **26**, 112 (1932); Black, W. C., Desavitsch, E. C., Trevorrow, V. E., and Lewis, R. C., *Ibid.*, **28**, 699 (1933)).

²⁸¹ DeJust, L. H., *Rev. actinologie physiotherap.*, **6**, 1 (1931); (*Chem. Abs.*, **26**, 2793 (1932)).

²⁸² Mellanby, E., *Brit. Dental J.*, **45**, 545 (1924).

²⁸³ Mellanby, M., and Pattison, C. L., *Brit. Med. J.*, **I**, 507 (1932); (*Chem. Abs.*, **26**, 5127 (1932)). Mellanby, M., *Brit. Dental J.*, **62**, 241 (1937).

²⁸⁴ Agnew, M. C., Agnew, R. G., and Tisdall, F. F., *J. Am. Dental Assoc.*, **20**, 193 (1933), (*Chem. Abs.*, **28**, 5103 (1934)).

²⁸⁵ Anderson, P. G., Williams, C. H. M., Halderson, H., Summerfeldt, C., and Agnew, R. G., *J. Am. Dental Assoc.*, **21**, 1349 (1934), (*Chem. Abs.*, **28**, 7314 (1934)); Fish, E. W., *J. Physiol.*, **84**, 272 (1935). *Final Report of the Committee for the Investigation of Dental Disease, His Majesty's Stationery Office, London, 1936*; (*Chem. Abs.*, **31**, 3531 (1937); McBeath, E. C., *Am. J. Public Health*, **24**, 1028 (1934); *N. Y. J. Dentistry*, **8**, 217 (1938); (*Chem. Abs.*, **32**, 5874 (1938); McBeath, E. C., and Zucker, T. F., *J. Nutrition*, **15**, 547 (1938)).

²⁸⁶ Rosebury, T., and Karshan, M., *Arch. Path.*, **20**, 697 (1935).

²⁸⁷ Shelling, D. H., and Anderson, G. M., *J. Am. Dental Assoc.*, **23**, 840 (1936), (*Chem. Abs.*, **30**, 5624 (1936)).

²⁸⁸ Blackberg, S. N., and Berke, J. D., *J. Dental Res.*, **12**, 349 (1932); (*Chem. Abs.*, **26**, 5129 (1932)).

²⁸⁹ See also Templin, V. M., and Steenback, H., *J. Biol. Chem.*, **100**, 217 (1933); Schour, I., and Ham, A. W., *Arch. Path.*, **17**, 22 (1934), (*Chem. Abs.*, **28**, 2762 (1934)).

²⁹⁰ Rappaport, B. Z., Reed, C. I., Hathaway, M. L., and Struck, H. C., *J. Allergy*, **5**, 541 (1934); (*Chem. Abs.*, **28**, 7361 (1934)).

²⁹¹ Rappaport, B. Z., and Reed, C. I., *J. Am. Med. Assoc.*, **101**, 105 (1933).

²⁹² Cornel, M., *Giorn. ital. dermat.*, **76**, 89 (1935); *Ber. ges. Physiol. exptl. Pharmacol.*, **88**, 59; (*Chem. Abs.*, **31**, 8629 (1937)).

²⁹³ Klein, S. J., *J. Bacteriol.*, **26**, 215 (1933).

²⁹⁴ Montgomery, B. E., *Proc. Soc. Exptl. Biol. Med.*, **28**, 481 (1930).

²⁹⁵ Greene, M. R., *Am. J. Hyg.*, **17**, 60 (1933); (*Chem. Abs.*, **27**, 1661 (1933)).

in an extensive study, was unable to detect any effect of a deficiency in vitamin D upon the ability of animals to produce antibodies or to resist infections. This is also the conclusion of Hess.²⁹⁶

Notwithstanding these generally negative results, there have been papers purporting to show that D increases the resistance to infection. Robertson and Ross²⁹⁷ found rachitic rats receiving *B. enteriditis* orally showed a 5 per cent survival when the diet contained non-irradiated and 30 per cent survival when it contained irradiated whole wheat. Similar effects also were described as due to the direct irradiation of the rat through Vitaglass. Koboshi²⁹⁸ found subcutaneous injections of staphylococci to produce more serious effects in rats deprived of vitamins A and D than in normal animals. Doses of Vigantol prevented the appearance of abscesses. Choun²⁹⁹ believed a high-vitamin diet to increase the resistance of guinea pigs to diphtheria. Pfannenstiehl³⁰⁰ noted a decreased germicidal power of the blood for typhoid organisms in D avitaminosis. Kemmler³⁰¹ found skin wounds to heal more rapidly when an irradiated ergosterol solution was applied directly. Pritchett³⁰² believed the resistance of mice on a normal diet to infection with paratyphoid bacillus or mouse typhoid bacillus to be increased by the addition of butter fat, cod-liver oil or by the use of irradiated milk.

It has been suggested that viosterol may be of value in the treatment of lead poisoning, since in cats large doses increase the excretion of that metal.³⁰³

Irradiated ergosterol is also asserted to increase the thrombocytes in blood and to reduce the coagulation time.³⁰⁴ It, as well as ultraviolet irradiation, tends to produce an increase in the fibrinogen and a decrease in the antithrombin content of the blood of newborn infants.³⁰⁵ Leopold, Bernhard and Tow³⁰⁶ report the lipids of the blood of children to be increased after ultraviolet irradiation, although the lipoid-phosphorus content is not changed. Nakae³⁰⁷ finds in rabbits that the daily administration of 0.1 to 1.5 cc. of irradiated ergosterol preparations decreases the serum cholesterol by about 40% in a month. Blood catalase is increased by small doses but decreased by an excess of vitamin D, according to Jusatz.³⁰⁸ Feeding moderate amounts does not affect the glutathione level in the blood, but after toxic doses, although the number of red cells is increased, each cell has a reduced glutathione content.³⁰⁹

It seems well established that metabolism is increased by vitamin D. Handovsky³¹⁰ found irradiated ergosterol to increase the oxygen consumption of

²⁹⁶ Hess, A. F., *New England J. Med.*, **207**, 367 (1932). See, however, Holm, R., *Z. Immunitäts*, **82**, 479 (1934); *Chem. Abs.*, **28**, 7346 (1934). For a general review, see Clausen, S. W., *Physiol. Rev.*, **14**, 309 (1934); Robertson, E. C., *Medicine*, **13**, 123 (1934).

²⁹⁷ Robertson, E. C., and Ross, J. R., *Proc. Soc. Exptl. Biol. Med.*, **27**, 999 (1930), **28**, 443 (1931).

²⁹⁸ Koboshi, S., *J. Chosen Med. Assoc.*, **23**, 39 (1933); *Chem. Abs.*, **28**, 4453 (1934).

²⁹⁹ Choun, C. K., *Z. Immunitäts*, **81**, 432 (1934), *Chem. Abs.*, **28**, 5505 (1934).

³⁰⁰ Pfannenstiehl, W., *Sitzber. Ges. Beförder ges. Naturw. Marburg*, **67**, 71 (1932); *Chem. Abs.*, **28**, 5507 (1934).

³⁰¹ Kemmler, H., *Mittl. Grenzgeb. Med. Chir.*, **43**, 453 (1934); *Chem. Abs.*, **29**, 5927 (1935).

³⁰² Pritchett, I. W., *J. Exptl. Med.*, **46**, 557 (1927).

³⁰³ Flinn, F. B., and Smith, A. R., *J. Ind. Hyg.*, **15**, 156 (1933); *Chem. Abs.*, **27**, 3529 (1933).

³⁰⁴ Phillips, R. A., Robertson, D. F., Corson, W. C., and Irwin, G. F., *Ann. Int. Med.*, **4**, 1134 (1931); *Chem. Abs.*, **25**, 5210 (1931).

³⁰⁵ Sanford, H. N., Gasteyer, T. H., and Wyatt, L., *Am. J. Diseases of Children*, **43**, 566 (1932); *Chem. Abs.*, **26**, 3560 (1932); Babasaki, Y., *Folia Pharmacol. Japon.*, **14**, 1 (1932); *Chem. Abs.*, **26**, 4100 (1932).

³⁰⁶ Leopold, J. S., Bernhard, A., and Tow, A., *Am. J. Diseases of Children*, **43**, 882 (1932); *Chem. Abs.*, **26**, 4350 (1932).

³⁰⁷ Nakae, R., *Nagoya J. Med. Sci.*, **7**, 88 (1933); *Chem. Abs.*, **28**, 3457 (1934).

³⁰⁸ Jusatz, H. J., *Klin. Wochschr.*, **11**, 1501 (1932); *Chem. Abs.*, **27**, 1030 (1933).

³⁰⁹ Hesse, H., *Biochem. Z.*, **268**, 304 (1934).

³¹⁰ Handovsky, H., *Arch. Exptl. Path. Pharmacol.*, **159**, 383 (1931); *Chem. Abs.*, **25**, 4053 (1931).

liver sections *in vitro*. Dhar³¹¹ has suggested that vitamin D may be essential to the proper oxidation of fats in the body. In infants with rickets or tetany, Nitschke and Schneider³¹² observed a lowered metabolic rate, which could be made to rise by giving the vitamin. Reed, Thacker, Dillman and Welch³¹³ found large doses of irradiated ergosterol to increase the metabolic rate of normal dogs. Landelium and Ljungkvist³¹⁴ have confirmed the ability of the vitamin to increase the depressed oxygen consumption of rachitic rats. Reed³¹⁵ found the administration of 20,000 to 552,000 I.U. daily, as Viosterol, to rats in two to six days caused first a marked increase in the metabolic rate, followed by a decrease and an irregular return to normal. On the other hand, Massaroli,³¹⁶ using the metadinitrobenzene method, found irradiated ergosterol to slow down the oxidation-reduction processes of the tissues. An increase may be observed in the respiration of the skin, according to Presnell.³¹⁷ It is said that the injection of irradiated (but not of unirradiated) ergosterol into the gall bladder of guinea pigs causes adenoid growths.³¹⁸

It has been stated that irradiated cholesterol accelerates alcoholic fermentation in brewing, although non-irradiated cholesterol inhibits it.³¹⁹

³¹¹ Dhar, N. R., *J. Phys. Chem.*, **36**, 1846 (1932).

³¹² Nitschke, A., and Schneider, M., *Z. Kinderheilk.*, **54**, 1 (1932); *Chem. Abs.*, **27**, 5399 (1933).

³¹³ Reed, C. I., Thacker, E. A., Dillman, L. M., and Welch, J. W., *J. Nutrition*, **6**, 355 (1933), *Chem. Abs.*, **27**, 5785 (1933).

³¹⁴ Landelium, E., and Ljungkvist, G., *Skand. Arch. Physiol.*, **68**, 252 (1934); *Chem. Abs.*, **28**, 4460 (1934).

³¹⁵ Reed, C. I., *Proc. Exptl. Biol. Med.*, **32**, 274 (1934).

³¹⁶ Massaroli, P., *Riv. pat. Sper.*, **10**, 1 (1933); *Chem. Abs.*, **28**, 3457 (1934).

³¹⁷ Presnell, A. K., *J. Biol. Chem.*, **121**, 5 (1937).

³¹⁸ Schmidt, H. O., *Z. Krebsforsch.*, **45**, 335 (1937); *Chem. Abs.*, **31**, 5874 (1937)

³¹⁹ De Fazi, R., and Pirrone, F., *Ann. Chim. Applicata*, **21**, 419 (1931); *Chem. Abs.*, **26**, 799 (1932); Pirrone, F., *Ann. Chim. Applicata*, **22**, 731 (1932); *Chem. Abs.*, **27**, 1916 (1933), Mameli, E., and Mossini, A., *Giorn. Chim. Ind. Applicata*, **16**, 377 (1934), *Chem. Abs.*, **28**, 7415 (1934)

Chapter 40

Commercial Production of Vitamin D

Rickets is now recognized to be an extremely widespread disease, its incidence being as high as 50 to 75 per cent. This is because milk, the chief food of the infant, is relatively low in antirachitic potency. Eggs and fish are practically the only foods which contain large amounts of the necessary food factor. Vegetables are entirely lacking in it.¹ For this reason, the discoveries described in the preceding chapters quickly found application in the preparation of infant foods, pharmaceutical products and in improving the dietetic value of milk. In the preparation of poultry foods, the various methods of introduction of the vitamin have been of great economic importance.

Notwithstanding the fact that the process of irradiation of foodstuffs was discovered in the United States, its widespread adoption, at least in the case of dried milk and the production of pharmaceutical solutions containing irradiated sterols, seems to have come about first in Germany, where György reported on the value of irradiated milk as early as 1926. The earliest commercial milk irradiation was conducted in Frankfurt by Scheer and in Basel by Wieland.² Irradiated Dryco has been manufactured in the United States since about 1927: Steenbock applied for a patent on June 30, 1924, and this was issued in the United States³ and assigned to the University of Wisconsin Alumni Research Foundation. By 1929, this foundation had licensed five drug manufacturers to produce irradiated sterol preparations.⁴ By November, 1929, the American Medical Association had approved the name Viosterol for such preparations. At about this time, licenses were also granted for the irradiation of milk and various cereal preparations. In England, a Steenbock patent⁵ made mention of the possibility of harmful overirradiation and stated that this could be avoided by limiting the time of exposure. The patent also included the separation of non-saponifiable lipids from fats either before or after the irradiation and their incorporation into foods. This included the preparation and irradiation of sterols and their esters obtained from such plant materials as yeast, molds, mushrooms, ergot, various seeds and straw, as well as from brain and other animal sources. In other U. S. Patents,⁶ he described the irradiation of cereals or solid cereal products to a regulated degree to develop antirachitic properties without subsequent injury to either these properties or to the palatability, by strictly limiting the time.

There are a number of other patents dealing with irradiation processes. Tillisch,⁷ claimed that irradiation of oils and fats produced, in addition to the antirachitic vitamin,

¹ Hess, A. F., "Rickets, including Osteomalacia and Tetany," p. 102, Philadelphia, Lea and Febinger, 1929.

² See also György, P., *Klin. Wochschr.*, 5, 747 (1926); 4, 1118 (1925).

³ Steenbock, H., U. S. P. 1,680,818, Aug. 14, 1928, to Wisconsin Alumni Research Foundation.

⁴ *Drug Markets*, 24, 347 (1929).

⁵ Steenbock, H., British P. 236,197, June 30, 1924; *J. Soc. Chem. Ind. Suppl.*, B, 735 (1925), 314,942, July 5, 1928; *Chem. Abs.*, 24, 1411 (1930).

⁶ Steenbock, H., U. S. P. 1,871,135-6, Aug. 9, 1932, to Wisconsin Alumni Research Foundation; *Chem. Abs.*, 26, 5675 (1932); German P. 605,960, Nov. 22, 1934, *Chem. Abs.*, 29, 1862 (1935).

⁷ Tillisch, H. C. E., British P. 270,296, April 28, 1926; *Chem. Abs.*, 22, 1415 (1928).

the fat-soluble A if oxygen was excluded. This is now known not to be possible. The harmful effects of ozone were eliminated through the use of a calcspar filter in the method of Heinemann,⁸ and Scholl⁹ attained the same objective when he displaced the air from an irradiated liquid by the passage of an inert gas. Stamsö¹⁰ increased the antirachitic potency of food oils, such as peanut oil, intended for a butter substitute, by irradiating it in thin layers with the exclusion of air, or by immersing lamps in the flowing liquid for not more than an hour. This was reduced to ten minutes in a later patent.¹¹ In other patents, there were many indefinite claims for the improvement of food products, without particular mention of the development of antirachitic potency, although this was undoubtedly the objective intended; the claims related to various details of the methods employed. Pacini¹² used rays other than those in the ultraviolet range, particularly infrared rays, or, in another patent,¹³ rays longer than 3022A for the treatment of many substances such as bacilli, molds, sarcoma tissue, and ergot, said to contain a growth vitamin.

During ultraviolet irradiation of foodstuffs, Ried¹⁴ employed a simultaneous irradiation either with x-rays or with wave-lengths longer than ultraviolet. Kelly¹⁵ similarly proposed the simultaneous or subsequent application of cathode rays. The use of the latter alone was claimed by Knudson.¹⁶ Sperti¹⁷ claimed the use of soft x-rays.

Perino¹⁸ described the use of an alkali monohydrogen phosphate solution in conjunction with the ultraviolet irradiation of various types of vegetable material.

Another type of patent covered the use of only restricted wave-length regions within the ultraviolet range in order to control the processes in such a manner as to avoid the accumulation of undesirable products or the destruction of the vitamin once it had formed. Thus, Sperti, Withrow, Norris and Schneider¹⁹ described a process for simultaneously increasing the vitamin content and destroying bacteria in which foods are irradiated with ultraviolet light with the exclusion, by suitable filters, of those shorter wave-lengths which are harmful to the taste, smell and color of the food. Chesney²⁰ places the threshold for destructive effects in the irradiation of foods at about 2900A and avoids the action of shorter wave-lengths by employing concentrated sunlight or skylight. Bills²¹ described an apparatus for exposing materials on a belt conveyor to sunlight filtered through a covering material such as Cellophane which is transparent to ultraviolet rays.

Reiter²² used only radiations longer than 2800A in irradiating substances containing ergosterol to avoid the formation of toxic products. It is now recognized that this cannot be accomplished since D₂ itself has toxic properties, but the

⁸ Heinemann, F., German P. 530,877, Nov. 4, 1926; *Chem. Abs.*, **26**, 221 (1932).

⁹ Scholl, H., French P. 646,792, Dec. 28, 1927; *Chem. Abs.*, **23**, 2106 (1929); British P. 283,472, Jan. 9, 1928; *Chem. Abs.*, **22**, 4015 (1928); Canadian P. 285,853, Dec. 25, 1928; *Chem. Abs.*, **23**, 1231, 2330 (1929).

¹⁰ Stamsö, K. K., British P. 246,473, Jan. 26, 1925; *Chem. Abs.*, **21**, 465 (1927).

¹¹ Stamsö, K. K., Swedish P. 72,502, Aug. 25, 1931; 72, 613, Sept. 8, 1931; *Chem. Abs.*, **27**, 3294 (1933).

¹² Pacini, A. J., British P. 296,053, Aug. 24, 1927; *Chem. Abs.*, **23**, 2252 (1929).

¹³ Pacini, A. J., U. S. P. 1,681,120, Aug. 14, 1928, to C. N. Richter; *Chem. Abs.*, **22**, 3737 (1928).

¹⁴ Ried, O., Austrian P. 121,657, Oct. 13, 1930; *Chem. Abs.*, **25**, 3130 (1931); see also for the preservation of foods in this way, the Fromray Co., British P. 325,824, *Chem. Abs.*, **24**, 3952 (1930), German P. 551,290.

¹⁵ Kelly, T. D., British P. 293,255, Nov. 28, 1927; *Chem. Abs.*, **23**, 1698 (1929).

¹⁶ Knudson, A., British P. 292,926, June 24, 1927; *Chem. Abs.*, **23**, 1446 (1929).

¹⁷ Sperti, G., U. S. P. 1,982,028, Nov. 27, 1934, General Development Laboratories, Inc.; *Chem. Abs.*, **29**, 517 (1935).

¹⁸ Perino, J., British P. 279,487, Oct. 20, 1926; *Chem. Abs.*, **22**, 2799 (1928); German P. 535,411; U. S. P. 1,754,434, April 15, 1930.

¹⁹ Sperti, G., Withrow, R., Norris, R., and Schneider, H., U. S. P. 1,982,029, Nov. 27, 1934, to General Development Laboratories, Inc.; *Chem. Abs.*, **29**, 517 (1935). There is now available a vegetable oil solution of ergosterol prepared in this manner containing 10,000 units per gram. Ridel, T., Sperti, G., Goode, P., and Cassidy, H., *J. Am. Med. Assoc.*, **106**, 452 (1936).

²⁰ Chesney, J. W. D., U. S. P. 1,704,173; *Chem. Abs.*, **23**, 1967 (1929); British P. 310,802, April 30, 1928.

²¹ Bills, C. E., U. S. P. 1,877,382, Sept. 13, 1932; *Chem. Abs.*, **27**, 4 (1933).

²² Reiter, T., French P. 697,367, Jan. 30, 1930; *Chem. Abs.*, **25**, 3131 (1931); British P. 342,500, Jan. 17, 1930.

formation of other inert toxic substances can be lessened. Most of the patents dealing with the use of filtered radiations were applied for before or shortly after the appearance of the work of Reerink and van Wijk, discussed in the preceding chapter. A study of this will aid in the evaluation of claims for the action of specific wave-lengths. Reiter's claims were in part based upon his observation²³ that, in the irradiation of milk, it is the wave-lengths between 2400 and 2800A which cause the undesirable changes in odor and taste.²⁴

The Philips Gloeilampenfabriken²⁵ proposed to increase the efficiency by filtering out wave-lengths shorter than 2700A by the use of a 10-mm. layer of a 5 per cent benzene solution, or *p*-xylene.

Campsie²⁶ eliminated infrared rays and used a cold quartz lamp giving chiefly the band 2537-2540A, the resonance lines of mercury, radiations which most authorities would agree would have to be very carefully limited in their application if destruction of the antirachitic substance is to be avoided.

The use of the carbon arc for irradiating foods was described by Chaney.²⁷ The formation of ozone which gives off-flavor, is particularly avoided by the use of electrodes²⁸ containing added iron or aluminum so that the energy emitted will have a high proportion of wave-lengths between 2000 and 3000A, with only a negligible portion shorter than 2000A.

It is not possible to discuss in detail the many patents dealing with the structural features of irradiation apparatus.²⁹

Shumway³⁰ removes the husk or skin from a cereal such as wheat, corn, oats, rye, barley or rice, and separates any pulverulent material, after which the whole cereal kernels are irradiated. Dorcas³¹ described the apparatus commonly used for irradiating such foods. A thin layer of the product an eighth of an inch deep flows on a moving belt before an ultraviolet lamp.

Jaeger³² described a therapeutic product prepared by irradiating dry banana meal in thin layers.

Berndt and Creighton³³ treat an opaque food substance at rest by ultraviolet rays only long enough to render a fraction of it antirachitic. This is then mixed with the untreated portion, again irradiated, the mixing and irradiation processes being alternately repeated, the total treatment received during the exposures of the fractions being less than the time required to impart undesirable properties to any portion.

²³ Reiter, T., *Naturwiss.*, **17**, 876 (1929); Kisch, E., and Reiter, T., *Strahlentherapie*, **39**, 452 (1930-31); Genin, G., [*Last*, **17**, 47 (1937); *Chem. Abs.*, **31**, 7494 (1937)] avoids rays less than 2600A.

²⁴ See also Weckel, K. G., Jackson, H. C., Haman, R., and Steenbock, H., *Wis. Agr. Expt. Sta., Bull.* **435**, 68 (1936); *Chem. Abs.*, **32**, 2633 (1938).

²⁵ N. V. Philips Gloeilampenfabriken, British P. 343,528, Sept. 14, 1929; French P. 700,312; *Chem. Abs.*, **25**, 3776 (1931).

²⁶ Campsie, H. G., U. S. P. 1,980,971, Nov. 13, 1934; *Chem. Abs.*, **29**, 498 (1935).

²⁷ Chaney, N. K., U. S. P. 1,842,313, Jan. 19, 1932 (to National Carbon Co.).

²⁸ Chaney, N. K., U. S. P. 1,894,158; *Chem. Abs.*, **27**, 2504 (1933).

²⁹ Geffcken, H. H., and Richter, H., German P. 523,257, Feb. 8, 1927; 526,141, May 17, 1929; Goodall, F. E., and van Sant, R. H., U. S. P. 1,735,610, Nov. 12, 1930. N. V. Philips Gloeilampenfabriken, British P. 313,558, June 14, 1928; *Chem. Abs.*, **24**, 1036 (1930). Hickman, J. O., British P. 392,626, Feb. 17, 1932; Tixier, G., British P. 376,996, July 21, 1932; Ross, J. C., U. S. P. 1,896,379; Zecher, G., U. S. P. 1,929,910, Oct. 10, 1933; *Brit. Chem. Abs.*, **B**, 587 (1934); Mailey, R. D., U. S. P. 1,969,655, Aug. 7, 1934; Ban, N., van Recsey, N., and van Recsey, E., British P. 382,349, Oct. 27, 1932; Brown, G., British P. 294,502, July 22, 1927; *Chem. Abs.*, **23**, 1967 (1929); Stephens, H. C., and Hoar, S. B., U. S. P. 2,020,250; Salmony-Karsten, A., *Allgem. Oel-und Fett-Z.*, **32**, 358 (1935); Beardslee, F. C., U. S. P. 1,682,318; Linder, J., Austrian P. 125,772, July 15, 1931; Soc. anon. des usines Rémy, Belgian P. 386,419, March 31, 1932; *Chem. Abs.*, **27**, 1416 (1933).

³⁰ Shumway, E. D., U. S. P. 1,928,397 (to Quaker Oats Co.), *Chem. Abs.*, **27**, 5840 (1933).

³¹ Dorcas, M. J., *Food Industries*, **1**, 504 (1929); *Chem. Abs.*, **32**, 4508 (1929).

³² Jaeger, C., British P. 290,195, April 18, 1928; *Chem. Abs.*, **23**, 916 (1929).

³³ Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8 (to R. U. V. Engineering Corporation); *Chem. Abs.*, **31**, 773, 2701 (1937).

A process for making biscuits, cakes, etc. in the presence of ultraviolet light was described by Elias,³⁴ and an apparatus for irradiating bread was described by Kielwein.³⁵ McGroarty³⁶ proposes the irradiation of an emulsified mixture prepared from salt, sugar, milk, shortening and yeast. This is then to be mixed with an irradiated yeast suspension, flour and water, for preparing bread dough. Antirachitic biscuits, prepared either from a dough with an added vitamin D concentrate or by the irradiation of the biscuits, retain their potency even after baking at 180-200°C. according to Markar'yan.³⁷ Tisdall³⁸ prepares biscuits, cakes, rusks or breads containing vitamins A, B, E and D from bone meal, baking powder and irradiated wheat germ, whole wheat and yeast.

Detailed studies of the antirachitic potency imparted to soda crackers by exposures at 12 inches, from a mercury arc emitting 94 ergs per second per sq. mm. have been reported by Read and Bailey.³⁹ Activation was attained in ten seconds, according to the results of bone-ash data on animals which had been on diets containing the crackers at a 20 per cent level. In the preparation of the crackers, lard, which may contain an appreciable amount of vitamin D, was replaced by hydrogenated shortening or lards shown to lack the vitamin. It was also shown that crackers made with irradiated shortening carried their antirachitic potency through the fermentation and baking processes.

Greaves and Nielson⁴⁰ find that the addition of 0.5 gm. of irradiated Utah-grown wheat causes a slight healing in rachitic rats. This becomes pronounced with 0.75 gm. or with 1.25 gms of the unirradiated wheat. The highest provitamin content was found in the Baart and the lowest in the Kharkov varieties. Becker⁴¹ studied the amounts of the vitamin which could be produced per hour in wheat, rye, barley, corn, peanut, linseed, sunflower-seed and pumpkin-seed meals. With the feed stationary, and exposures of 10 to 120 seconds, 160 to 1360 units were produced and in feed moving beneath the lamp in a thin layer, 1500 to 18,000 I.U. A reasonable speed is that allowing an activation of about 0.5 I.U. per gram.

The addition of 10 per cent of irradiated farina in the diet of the rat failed to cause healing of rickets in experiments by Schlutz and Ziegler.⁴² Pincussen⁴³ believes that irradiated oats stimulate carbohydrate metabolism in rabbits. The administration of irradiated cereals to school children produced no increase in calcium and phosphorus retention beyond the limits of normal variation, according to Porter-Levin.⁴⁴ Drake and Tisdall⁴⁵ found that irradiated farina given to children on a low calcium diet caused an increased efficiency in the utilization of these elements. Autoclaving an irradiated ration for six hours at fifteen lbs. does not affect its antirachitic properties.⁴⁶

Ultraviolet rays impart antirachitic value to lettuce, alfalfa, spinach and soybeans, but not to cabbage.⁴⁷ Greater antirachitic properties are imparted to the cut than to the intact plant, but the exposures necessary to produce the vitamin in the plant are longer than those required to produce enough to protect a directly irradiated animal.

The irradiation of three kinds of mushrooms, as well as of the autoclaved, dried

³⁴ Elias, O. A., *British P.* 266,101, Jan. 12, 1926

³⁵ Kielwein, F., *German P.* 564,401, Nov. 1, 1927; 608,277, Jan. 19, 1935; *Chem. Abs.*, 29, 2618 (1935); *German P.* 647,522, July 6, 1937; *Chem. Abs.*, 31, 8739 (1937)

³⁶ McGroarty, W. J., U. S. P. 1,863,277; *Chem. Abs.*, 26, 4111 (1932)

³⁷ Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U S S R.* 1, 198 (1936); *Chem. Abs.*, 31, 1854 (1937).

³⁸ Tisdall, F. F., *British P.* 357,223, Jan. 24, 1930; *Chem. Abs.*, 27, 350 (1933).

³⁹ Read, J. W., and Bailey, C. H., *Cereal Chemistry*, 10, 99 (1933); *Chem. Abs.*, 27, 2982 (1933); Wörner, A., [U. S. P. 1,796,134; *Chem. Abs.*, 25, 2493 (1931)] claims to avoid impairment of the taste of bread by using a reflector and permitting no direct rays to strike the bread

⁴⁰ Greaves, J. E., and Nielson, H., *Food Research*, 1, 495 (1936); *Chem. Abs.*, 31, 2647 (1937).

⁴¹ Becker, J., *Mezőgazdasági Kutatások*, 9, 191 (1936); *Chem. Abs.*, 30, 7701 (1936).

⁴² Schlutz, F. W., and Ziegler, M. R., *J. Am. Med. Assoc.*, 93, 1466 (1929); for further experiments on irradiated cereals, see Steenbock, H., Black, A., and Thomas, B. H., *J. Biol. Chem.*, 85, 585 (1930).

⁴³ Pincussen, L., *Strahlentherapie*, 51, 685 (1934); *Chem. Abs.*, 29, 4051 (1935).

⁴⁴ Porter-Levin, T., *J. Am. Diet. Assoc.*, 8, 482 (1933); *Chem. Abs.*, 27, 2986 (1933)

⁴⁵ Drake, T., and Tisdall, F. F., *Canadian Med. Assoc. J.*, 26, 296 (1932); *Chem. Abs.*, 27, 4278 (1933).

⁴⁶ Daniels, A. L., and Jordan, D. P., *Proc. Soc. Exptl. Biol. Med.*, 26, 453 (1929).

⁴⁷ Lolkin, M., *Contributions Boyce Thompson Inst.*, 3, 245 (1931); *Chem. Abs.*, 25, 5450 (1931).

and ground pad resulting from the growth of certain molds in an inorganic medium containing 4 per cent of glucose, produces the vitamin, according to Preuss, Peterson, Steenbock and Fred.⁴⁸

June butter fat is a poor source of vitamin D but is readily activatable, a ten-minute exposure at a depth of 1.6 mm. being best.⁴⁹ It would also be possible to improve its quality by the introduction of irradiated ergosterol. Lampitt, Sylvester and Bilham⁵⁰ have described a method for the irradiation of fats in which the light reaching the cell containing the fat is standardized by the use of a simultaneously exposed calibrated photoelectric cell. This arrangement, although employed for the study of oxidation processes, would also be applicable to the formation of the vitamin.

Nomura⁵¹ proposed to ferment mixtures of flour, fruit juices, Japanese yams, and meat or fish soup, and then irradiate, dry and powder the product.

Favorable results with irradiated chocolates were reported by Krasso.⁶² McKinlay⁵³ exposed chocolate candy on an endless belt to a mercury arc. Ried⁵⁴ ascribed beneficial effects to the irradiation of added metals or compounds such as zinc oxide, ferrous carbonate or calcium carbonate mixed with the fatty materials in the chocolate.

Labbé⁵⁵ extracted sterols from cacao beans, separated the α - and β - sterols by crystallization, mixed and irradiated them.⁵⁶

Drummond,⁵⁷ in discussing the public health aspects of the vitamin D fortification of foodstuffs, concludes that their promiscuous irradiation is of questionable value. He did, however, consider the addition of calciferol to milk to be justified. Another discussion involving the status of the problem of vitamin addition to foods in general use has been given by Sherman and others.⁵⁸ The possibilities of the production of vitamin D have been extended by extravagant claims. Thus, it has been proposed to impregnate textiles with materials which, upon irradiation, acquire therapeutic properties.⁵⁹

Pharmaceutical Developments. The value of pharmaceutical preparations of D₂, Viosterol, is firmly established, and, since its use is less apt to be promiscuous, is less subject to criticism than is the general irradiation of foodstuffs. At first it was believed that the antirachitic or growth-promoting properties of cod-liver oil could be enhanced by irradiation,⁶⁰ but, as stated in the preceding chapter it is now generally recognized that the oil contains little, if any, provitamin and the effects of irradiation can only be to destroy the vitamins A and D₃ naturally present.⁶¹ However, Coster and Günther⁶² maintained that the antirachitic potency once destroyed in the hardening of cod-liver oil may be restored by irradiation.

⁴⁸ Preuss, L. M., Peterson, W. H., Steenbock, H., and Fred, E. B., *J. Biol. Chem.*, **90**, 369 (1931).

⁴⁹ Steenbock, H., Wirick, A. M., and Rusing, B. M., *J. Dairy Sci.*, **13**, 497 (1930); *Chem. Abs.*, **25**, 729 (1931).

⁵⁰ Lampitt, L. H., Sylvester, N. D., and Bilham, P., *Biochem. J.*, **29**, 1167 (1935).

⁵¹ Nomura, R., French P. 701,808, Sept. 9, 1930; *Chem. Abs.*, **25**, 4068 (1931).

⁵² Krasso, H., *Wiener Klin. Wochschr.*, **42**, 898 (1929); *Chem. Abs.*, **23**, 5238 (1929).

⁵³ McKinlay, D., British P. 276,860, Oct. 27, 1926; *Brit. Chem. Abs.*, **B**, 858 (1927); see also Oppenheim, E., British P. 309,601, April 13, 1928, Swiss P. 142,862, April 9, 1929; French P. 672,318, March 29, 1929; *Chem. Abs.*, **24**, 2213 (1930).

⁵⁴ Ried, O., British P. 316,264, July 26, 1928, *Chem. Abs.*, **24**, 1683 (1930); *Wiener Klin. Wochschr.*, **42**, 896 (1929); *Chem. Abs.*, **23**, 5218 (1929); Austrian P. 126,148, Aug. 15, 1931; 123,648, Dec. 15, 1929.

⁵⁵ Labbé, H., French P. 700,036, Nov. 16, 1929; *Chem. Abs.*, **25**, 3409 (1931).

⁵⁶ See also for chocolate irradiation, the patents of the van Houten Co., British P. 340,580, Nov. 24, 1928; French P. 68,093.

⁵⁷ Drummond, J. C., *Chemistry and Industry*, 744 (1935).

⁵⁸ *Am. Public Health Assoc. Yearbook*, 78 (1933-4). For the engineering aspects, Gunderson, F. L., *Cereal Chem.*, **7**, 449 (1930); *Chem. Abs.*, **25**, 131 (1931). Krauss, E., and Bethke, R. M., [*Ohio Agr. Expt. Sta., Bimonthly Bull.*, **184**, 3 (1937); *Chem. Abs.*, **31**, 5886 (1937)] believe the addition of the vitamin to foods should be limited to milk. See also Fleisch, A., *Presse méd.*, **45**, 1542 (1937); *Chem. Abs.*, **32**, 3797 (1938); Knapp, A. W., *Chemistry and Industry*, 558 (1938).

⁵⁹ Lederer, B., French P. 796,046, March 27, 1936; *Chem. Abs.*, **30**, 5727 (1936).

⁶⁰ Price, W. A., *Am. J. Diseases of Children*, **33**, 78 (1927).

⁶¹ Van Leersum, E. C., *Nederland. Tijdschr. Geneesk.*, **74**, I, 899 (1930); *Chem. Abs.*, **24**, 3264 (1930).

⁶² Coster, J. H., and Günther, G., Austrian P. 124,892, May 15, 1931; *Chem. Abs.*, **26**, 761 (1932).

In England, the production of ergosterol on a large scale was begun about 1928 by the British Drug Houses, Ltd. and by the Boots Drug Co., Ltd.⁶³ When irradiated, it was employed in margarine manufacture and in pharmaceutical preparations, such as Radiomalt, a palatable preparation which also contained vitamins A and B, and Vitamalt.⁶⁴

Many of the patents cited in previous paragraphs apply also to the irradiation of ergosterol, but many more are concerned with this alone. Indeed, most of the developments discussed in the preceding chapter were patented. In the earlier period there were several claims which have since turned out to have little significance, or to be erroneous. The use of x-rays, cathode rays or corona discharges⁶⁵ apparently has not yet been widely applied. Claims have been made that the formation of the vitamin could be effected without the use of ultraviolet rays by treating ergosterol with metallic catalysts, such as copper, bronze and nickel.⁶⁶

It is not possible to discuss the structural details of apparatus utilized for irradiation. At one time it was stated that the irradiated solutions should be at temperatures above 70°C.⁶⁷ Bills⁶⁸ gave details of a method for repeatedly circulating the solution through a chamber between the quartz mercury burner and the lamp casing. Fraps⁶⁹ described methods used in exposing ergosterol to sunlight.⁷⁰

Trufanov⁷¹ agitates the solution of ergosterol in a water-cooled quartz vessel by a flow of carbon dioxide sucked through by a vacuum pump. He alters about 50 per cent of a 2 per cent solution of the sterol in benzene, using as a source a carbon arc at a distance of 5 cm., the electrodes being composed of 65 parts carbon, 2.5 iron and 32.5 magnesia.

From and others claim⁶² that infrared rays assist the formation of the vitamin by antibacterial rays from a glow discharge. They also provide means for circulating ozone. In addition, the use of dyes as sensitizers⁷² has been proposed, although these substances have been said to lead to the formation of substances different from the vitamin by Windaus (chapter 39).

Apparently, the earliest commercial irradiated ergosterol product was the toxic Vigantol (chapter 39), prepared by the aid of a photoelectric device which cut off the light when the maximum absorption of wave-lengths between 2400 and 2500Å had been attained.⁷⁴

⁶³ Langton, H. M., *J. Soc. Chem. Ind.*, **48**, 31 (1929).

⁶⁴ Reviews of recent applications: Tabern, D. L., *Clin. Med. Surg.*, **40**, 9 (1933); Weidlich, G., *Z. Vitaminforsch.*, **2**, 253 (1933); Tanret, G., *Bull. soc. chim. biol.*, **15**, 1346 (1933); Routh, I. B., *J. Chem. Educ.*, **10**, 13 (1933); Borgeaud, P., *Bull. Soc. Vaud. Sci. Nat.*, **58**, 17, 232 (1933).

⁶⁵ I. G. Farbenindustrie, British P. 318,269, April 2, 1928; *Brit. Chem. Abs.*, **B**, 711 (1929); Whittier, C. C., U. S. P. 2,106,779, 2,106,780-1-2, Feb. 1, 1938, *Chem. Abs.*, **32**, 2692 (1938); Kramer, B., Natelson, S., and Sobel, A. E., U. S. P. 2,112,242, March 29, 1938, *Chem. Abs.*, **32**, 3913 (1938); Milas, N. A., U. S. P. 2,117,100, May 10, 1938, *Chem. Abs.*, **32**, 5161 (1938) The product known as Ertron is made by the Whittier process.

⁶⁶ Heilbron, I. M., British P. 318,268, March 2, 1928, *Chem. Abs.*, **24**, 2244 (1930).

⁶⁷ I. G. Farbenindustrie, British P. 316,803, Sept. 17, 1928; *Chem. Abs.*, **24**, 1938 (1930).

⁶⁸ Bills, C. E., U. S. P. 1,808,760, June 9, 1931, *Chem. Abs.*, **25**, 4156 (1931).

⁶⁹ Fraps, R. M., U. S. P. 2,015,264-5, Aug. 24, 1935; *Chem. Abs.*, **29**, 7587 (1935).

⁷⁰ Other patents on irradiation apparatus: Buhtz, E., German P. 514,992, June 27, 1926, Cuny, L., German P. 637,716, Nov. 3, 1936, O'Brien, B., British P. 459,043 and 459,118, Dec. 28, 1936, *Chem. Abs.*, **31**, 4021 (1937); Pfeidemenges, H., British P. 638,338, July 27, 1927, Patent Treuhand Ges. für Elektrische Glühlampen, German P. 553,016, Dec. 21, 1927, 541,991, Oct. 30, 1927, Quarzlampen. Ges., British P. 295,023, Aug. 4, 1927; Nicholls, H. J., U. S. P. 2,070,307, *Chem. Abs.*, **31**, 2054 (1937); Tixier, G., British P. 356,083, Jan. 22, 1930; Zechei, G., U. S. P. 1,929,910, Vilenkin, M., Russian P. 25,652, March 31, 1932; *Chem. Abs.*, **26**, 5231 (1932); Hickman, J. O., British P. 392,626, May 29, 1933; Salmony-Karsten, A., *Kautschuk*, **10**, 55 (1934); *Milchwirtschaft Zentr.*, **63**, 225 (1934); *Chem. Abs.*, **29**, 236 (1935); Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395, Aug. 18, 1936.

⁷¹ Trufanov, A. V., *Khim. Farm. Prom.*, **196**, 253 (1933); *Chem. Abs.*, **28**, 498, 4108 (1934).

⁷² From, V. C., Rowley, C. D., and Larsky, A. W., British P. 325,824, Feb. 2, 1929.

⁷³ Merck, Chemische Fabrik, British P. 286,665, March 8, 1927, *Brit. Chem. Abs.*, **B**, 836 (1928), *Chem. Abs.*, **23**, 483 (1929).

⁷⁴ British P. 296,093, Aug. 22, 1928, to I. G. Farbenindustrie A.-G.; *Brit. Chem. Abs.*, **B**, 73 (1929).

Some have attempted to prevent losses during the irradiation by the use of certain additions to the solvent. Thus, ethylene or an alkali hydroxide has been added to ether or alcohol for this purpose.⁷⁵ Brauchli⁷⁶ uses hydroquinone or other dihydroxyphenols. To obtain stable solutions, Hooper⁷⁷ dissolves the highly active transformation product of ergosterol in 1,2—,2,3—,1,3— or 1,4-butanediol or 2-methyl-1, 3-propanediol. A method has been described for extracting the reaction product from the solvent after its exit from the reaction chamber, followed by the introduction of fresh provitamin into the solvent in the reaction chamber so that the solvent may be used repeatedly.⁷⁸ The acid esters of sterols may be irradiated before they are converted into salts.⁷⁹

Various methods have been proposed for separating the irradiation product. In one,⁸⁰ the unchanged ergosterol is separated by virtue of its small solubility in alcohol, acetone, etc. The separation is continued until the ergosterol shows a dextrorotatory power greater than 25° for the yellow line of mercury. The active material is obtained by distillation of the solvent. Light and Frey⁸¹ carry out the irradiation in solvents such as diethylene dioxide, triethanolamine, ethyl acetate, etc., which have a much higher solvent power for the activated product than for the original ergosterol. Jendrassik⁸² irradiated solid ergosterol in contact with a solution containing vitamin D or ergosterol. The solution formed was led away by dialysis and fresh solution continuously added.

Filters to eliminate various wave-lengths have been suggested. Some would remove, by a carbon disulfide filter, wave-lengths longer than 3000A, particularly the 3126 and 3132A lines of mercury, believing these to be harmful.⁸³

The work of Reerink and van Wijk, discussed in the preceding chapter, has also been made the basis of patents assigned to the Philips Lamp Works.⁸⁴ This, it may be recalled, eliminates wave-lengths shorter than 2700 and longer than 3000A.

Spectrographic control of the irradiation process is specified by Zimmermann and Frankenburger⁸⁵ much as in the earlier Vigantol patents, except that it is stated that the irradiation is to be interrupted before the maximal absorption between 2300 and 3000A has been exceeded.

⁷⁵ I. G. Farbenindustrie A.-G., British P. 321,992, Oct. 25, 1928; *Chem. Abs.*, **24**, 2837 (1930); British P. 316,803, Sept. 17, 1928; *Brit. Chem. Abs.*, **B**, 836 (1929); *Chem. Abs.*, **24**, 1938 (1930).

⁷⁶ Brauchli, E., U. S. P. 1,824,653, Sept. 22, 1931 (to Hoffman LaRoche, Inc.); *Chem. Abs.*, **26**, 181 (1932); British P. 334,002, July 1, 1929.

⁷⁷ Hooper, C. W., U. S. P. 2,030,792 (Winthrop Chemical Co.); British P. 436,713, Oct. 16, 1935; *Chem. Abs.*, **30**, 1949, 2326 (1936).

⁷⁸ I. G. Farbenindustrie A.-G., British P. 314,267, Aug. 20, 1928; Frankenburger, W., and Weizel, W., German P. 491,222, May 20, 1928; *Chem. Abs.*, **24**, 2056 (1930); French P. 675,558, May 10, 1929; *Chem. Abs.*, **24**, 2674 (1930); see also Merck, German P. 556,716, March 6, 1928, for a description of an aqueous, colloidal solution of irradiated ergosterol.

⁷⁹ Hoffman-La Roche Co., German P. 567,333, Dec. 13, 1928.

⁸⁰ Soc. des usines chimiques Rhône-Poulenc, British P. 335,377, March 27, 1930; 335,277, June 25, 1929; French P. 698,040, June 11, 1930; *Chem. Abs.*, **25**, 1562, 3039 (1931).

⁸¹ Light, R. F., and Frey, C. N., U. S. P. 1,955,554, (to Standard Brands), *Chem. Abs.*, **28**, 3752 (1934); British P. 394,408, June 29, 1933; Canadian P. 335,281, June 13, 1933; *Chem. Abs.*, **27**, 4631 (1933).

⁸² Jendrassik, A., Hungarian P. 104,227, April 14, 1931; *Chem. Abs.*, **27**, 1387 (1933).

⁸³ N. V. Philips' Gloeilampenfabrieken, French P. 714,827, April 4, 1931; *Chem. Abs.*, **26**, 1715 (1932); French P. 737,234, May 17, 1932; *Chem. Abs.*, **27**, 1453 (1933); French P. 700,312, July 17, 1930; *Chem. Abs.*, **25**, 3776 (1931); **27**, 810 (1933); Dutch P. 32,096, Feb. 15, 1934; *Chem. Abs.*, **28**, 3842 (1934); French P. 708,548, Dec. 29, 1930; British P. 385,626, Dec. 20, 1932. Some of these deal with methods for removal of portions of the solvent and for the addition of added amounts of ergosterol.

⁸⁴ Reerink, F. H., and van Wijk, A., U. S. P. 1,904,751, April 18, 1933, to N.-V. Philips' Gloeilampenfabrieken, *Chem. Abs.*, **27**, 3560 (1933); German P. 634,146, Aug. 18, 1936; *Chem. Abs.*, **30**, 8533 (1936).

⁸⁵ Zimmermann, W., and Frankenburger, W., U. S. P. 1,896,191 (Winthrop Chemical Co.); *Chem. Abs.*, **27**, 2534 (1933).

Much of the work of the Göttingen laboratories has been patented, the United States patents being held by the Winthrop Chemical Co. Windaus⁸⁶ described the preparation of D₂ by irradiating ergosterol with light excluding wave-lengths shorter than 2750 Å. About 40-50 per cent conversion was obtained. Unchanged ergosterol was removed and the product was treated with citraconic anhydride for ten days in ether solution. Removal of the solvent was effected by evaporation at a low temperature. The residue is then saponified with alcoholic potassium hydroxide, diluted with water after about 12 hours, extracted with ether, petroleum ether or both, washed with water and dried. Following the latter operation, the solvent is evaporated and the residue crystallized from alcohol. Linsert⁸⁷ uses the unfiltered light of a magnesium spark, the remaining treatment being very similar to that described by Windaus. In the earlier patents, he specified the use of maleic anhydride, which left the antirachitic products in solution. Subsequently, Linsert⁸⁸ described the removal of the D₂ by the use of *m*-dinitrobenzoyl chloride in the presence of pyridine.

There are a great number of patents dealing with the introduction of irradiated ergosterol into food products. Ernotte⁸⁹ states that an aqueous-oil emulsion of vitamin D may be made with lecithin as the emulsifier.

The recent attention to a cholesterol derivative as the true provitamin of the natural antirachitic vitamin has been reflected in a patent by Waddell,⁹⁰ who described methods of treating cholesterol by mild oxidation with hydrogen peroxide or benzoyl peroxide, or by heat treatment, in order to increase the provitamin content.

The sterols of duck eggs may be irradiated to obtain preparations of antirachitic value for chickens.⁹¹ Fats of various invertebrates may also be irradiated for this purpose.⁹²

The various irradiated ergosterol preparations are very widely used. Besides the simple vitamin D preparations, there are a great number of products in which the irradiated ergosterol is supplemented by various other vitamins. Practically all the preparations are assayed in terms of the international standard. During the early developments there were, however, considerable variations in the potency of the products, since they were assayed against samples of cod-liver oil, the potency of which was not guaranteed.⁹³

⁸⁶ Windaus, A., U. S. P. 1,873,942, Aug. 23, 1932; *Chem. Abs.*, 26, 6072 (1932); U. S. P. 1,902,745; *Chem. Abs.*, 27, 3294 (1933); German P. 565,900, April 3, 1931, and 583,791, Sept. 9, 1933. The last describes the conversion of ergosterol to D₂.

⁸⁷ Linsert, O., U. S. P. 1,902,785; *Chem. Abs.*, 27, 3294 (1933); German P. 576,021 and 565,900; British P. 405,321; 370,743, April 2, 1931, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 28, 4842 (1934).

⁸⁸ Linsert, O., German P. 603,088, Sept. 22, 1934; *Chem. Abs.*, 29, 552 (1935); U. S. P. 2,030,377; *Chem. Abs.*, 30, 2326 (1936). The irradiation of 22-dihydroergosterol is also described. I. G. Farbenindustrie, A.-G., German P. 642,759, March 16, 1937; *Chem. Abs.*, 31, 6417 (1937). U. S. P. 2,128,199, Aug. 23, 1938; *Chem. Abs.*, 32, 8702 (1938). For 7-dehydrocholesterol, see Windaus, A., and Schenck, F., U. S. P. 2,099,550, Nov. 16, 1937; *Chem. Abs.*, 32, 312 (1938). German P. 661,686, June 24, 1938; *Chem. Abs.*, 32, 8706 (1938). For irradiation of oxidized cholesterol, E. I. du Pont de Nemours and Co., British P. 485,452, May 17, 1938; *Chem. Abs.*, 32, 8081 (1938).

⁸⁹ Ernotte, M., French P. 796,101, March 30, 1936; *Chem. Abs.*, 30, 5676 (1936).

⁹⁰ Waddell, J., U. S. P. 2,028,364; *Chem. Abs.*, 30, 1521 (1936); U. S. P. 2,056,992; *Chem. Abs.*, 30, 8533 (1936). Pacini, A. J., U. S. P. 1,880,977-8; *Chem. Abs.*, 27, 567 (1933) proposed the irradiation in the presence of a sensitizer such as uranium acetate. Cf. the work of Windaus on the course of such reactions with dyes as sensitizers.

⁹¹ N. V. Philips' Gloeilampenfabrieken, British P. 464,066, April 12, 1937; *Chem. Abs.*, 31, 6417 (1937).

⁹² N. V. Philips' Gloeilampenfabrieken, British P. 471,994, Sept. 15, 1937; *Chem. Abs.*, 23, 1408 (1938); British P. 477,283, Dec. 22, 1937; *Chem. Abs.*, 32, 3913 (1938).

⁹³ See Holmes, A. D., and Pigott, M. G., *J. Biol. Chem.*, 64, 263 (1925); Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, 39, 44 (1930); De Sanctis, A. G., and Craig, J. D., *J. Am. Med. Assoc.*, 94, 1285 (1930). For assays of German preparations, see Heubner, W., and Frerichs, M., *Arch. expil. Path. Pharmacol.*, 165, 553 (1932); *Chem. Abs.*, 26, 5127 (1932).

METHODS FOR INCREASING VITAMIN D IN MILK.

Although rickets is not a fatal disease, it has serious consequences. Improved methods of treatment and a better understanding of the disease have lessened the number of cases in which obvious deformities have been produced. There remain many cases in which less evident skeletal changes of the chest may be produced which predispose to respiratory diseases and faulty development of the pelvic arch, the latter sometimes increasing the difficulties of childbirth. The high incidence of the disease has led to much recent work on the development of a safe, generally applicable prophylactic to be supplied in the nutrition of all infants of a community with the object of rendering subsequent treatment of the disease unnecessary. Since direct sunlight is not in all cases available in the winter months, and artificial irradiation of all infants is too expensive to be feasible, the vitamin must be supplied in the food. The only food given infants of the most susceptible age is milk, and for this reason it has been important to study its adequacy in the prophylaxis of rickets. Unfortunately, milk is low in antirachitic potency, having only about five to ten Steenbock units per quart, whereas an average infant requires 35 to 50, the equivalent of three teaspoons of cod-liver oil, in order to prevent the occurrence of rickets. According to Thomas and Cannon,⁹⁴ butter fat may contain about one Steenbock unit in 9 grams. Intensive work in the last few years has led to the proposal of a number of methods by which the antirachitic potency of milk may be rendered adequate.⁹⁵

These may be classified as follows:

- I. Treatment of the Cow
 - A. Irradiation
 - B. Addition of vitamin D to the food as
 1. Irradiated ergosterol
 2. Irradiated yeast
 3. Irradiated molds or other products
 4. Irradiated natural provitamin
 5. Concentrates from natural sources
- II. Treatment of the Milk
 - A. Addition of Vitamin D as
 1. Irradiated ergosterol
 2. Irradiated natural provitamin
 3. Concentrates from natural sources
 - B. Irradiation

Antirachitic milk has the vitamin in an essential food which also supplies the necessary calcium and phosphorus.⁹⁶

⁹⁴ Thomas, B. H., and Cannon, C. Y., *Iowa Agr. Exp. Sta. Report*, 26 (1933), *Chem. Abs.*, 29, 3002 (1935).

⁹⁵ General reviews are due to: Oser, B. L., *Milk Plant Monthly* 23, No. 10, 34 (1934); *Chem. Abs.*, 28, 7373 (1934); Tonney, F. O., *Am. J. Public Health*, 26, 665 (1936); Olson, T., and Wallis, G., *S. Dakota Agr. Exp. Sta. Bull.* 296, 3 (1935), *Chem. Abs.*, 30, 5666 (1936); Andresen, O., *Arch. Kinderheilk.*, 90, 65 (1930); *Chem. Abs.*, 26, 501 (1932); Weckel, K. G., *Milk Plant Monthly*, 23, No. 3, 27 (1934); *Chem. Abs.*, 28, 3490 (1934); Roadhouse, C. L., *Proc. 19th Ann. Meeting, Western Division Am. Dairy Sci. Assoc.*, 109 (1933); Ellington, E. V., *Proc. 6th Ann. State Coll. Washington Inst. of Dairying*, 17 (1933); Batchelder, E. L., *Ibid.*, 48; *7th Inst.*, 47 (1934); Auerbacher, L. J., *Med. J. Record*, Nov. 2, 16 (1932); Bunker, J., and Harris, R. S., *New England J. Med.*, 211, 1140 (1934); Shrader, J. H., *Arch. Phys. Therap. X-Ray, Radium*, 15, 709 (1934); *Chem. Abs.*, 29, 1861 (1935); Barnes, D. J., *Am. J. Diseases of Children*, 48, 1258 (1934); Toley, J. A., *8th Ann. Report N. Y. State Dairy and Milk Inspectors*, 107 (1934), *Chem. Abs.*, 29, 4465 (1935); Smith, C. A., *Milk Dealer*, 23, No. 10, 38 (1934); McCollum, E. V., *Ibid.*, 24, No. 4, 32 (1935); Kon, S. K., *J. Dairy Research*, 7, 192 (1936); Kramer, B., and Gittleman, I. F., *New England Med. J.*, 209, 906 (1933); Wyman, E. T., *Ibid.*, 889.

⁹⁶ Hess, A. F., *Am. J. Public Health*, 22, 121 (1932).

That the potency of a milk depends upon the amount of sunlight to which the cow has access has been known since the first observations of the formation of vitamin D by irradiation.⁹⁷ Monthly assays conducted over a two-year period by Bechtel and Hoppert⁹⁸ indicated variations of as much as 900 per cent in antirachitic potency of the milk fats. The values were highest in July, August and September and lowest in February. Apparently, exposure to sunlight is the factor determining the activity of the milk. Guernsey milk varied from 4.8 to 43.8 U.S.P. units per quart and Holstein milk from 3.1 to 27.7. Gabathuler⁹⁹ states that milk at Davos in the Swiss Alps is twice as rich in D as milk from the plains.

Somewhat negative indications regarding the efficacy of irradiation of the cow were reported by Steenbock,¹⁰⁰ who was, however, concerned with the calcium balance of the lactating cow rather than with the antirachitic potency of the milk. Gowen, Murray, Gooch and Ames¹⁰¹ reported that after daily exposures of cattle for fifteen to thirty minutes to ultraviolet rays, it was possible to cure rickets in chicks by feeding their milk. Similar results were reported by Falkenheim, Vöitz, and Kirsch.¹⁰² Hess, Weinstock and Sherman¹⁰³ found irradiation of a nursing human mother to increase the antirachitic potency of her milk.

Irradiation of cows has been said also to increase the milk production by 4.77 per cent and the butter fat by 8.73 per cent.¹⁰⁴ Büniger,¹⁰⁵ however, was unable to observe significant changes in the amount of milk, its fat content, or mineral content or vitamin content in cows confined in stalls and irradiated either on the back, udders or both back and udders. The daily doses used varied from ten minutes at 100 cm. to thirty minutes at 75 cm. The irradiation period lasted about two months.

In experiments of Mitchell, Eiman, Whipple and Stokes,¹⁰⁶ carbon arcs were hung so that the arc formed opposite the under side of the cow's body about midway from front to back, providing a good exposure of the udders and more tender side of the body. The arcs were about 25 inches from the animals and at this distance the total ultraviolet intensity between 2000 and 4000Å was 6400 microwatts per sq. cm. or 640 ergs per sq. mm. Each cow was irradiated for fifteen minutes each day on one side only. Rat assays gave an average of 22 units per qt. (controls 5 units per qt.) This milk had similar protective power on infants to irradiated milk, and appeared also to have curative power in florid rickets, although its action was somewhat slower than that of other antirachitic agents.

Hess pointed out that this method is suitable for carefully controlled herds producing certified milk. It may also be of value in smaller communities where large-scale equipment for the irradiation of milk appears to be too expensive.

It has been shown possible to increase the vitamin D content of butter fat

⁹⁷ Luce, E. M., *Biochem. J.*, **18**, 1279 (1924); Chick, H., and Roscoe, M. H., *Ibid.*, **20**, 632 (1926).

⁹⁸ Bechtel, H. E., and Hoppert, C. A., *J. Nutrition*, **11**, 537 (1936); *Chem. Abs.*, **30**, 6044 (1936); Campion, J. E., Henry, K. M., Kon, S. K., and Macintosh, J., *Biochem. J.*, **31**, 81 (1937).

⁹⁹ Gabathuler, A., *Z. Vitaminkunde*, **1** (1931); *Chem. Abs.*, **27**, 5102 (1933).

¹⁰⁰ Steenbock, H., Hart, E. B., Humphrey, G. C., Elvehjem, C. A., and Scott, H. T., *J. Biol. Chem.*, **67**, 371 (1926); Hart, E. B., Steenbock, H., and Scott, H. T., *Ibid.*, **66**, 441 (1925), **73**, 59 (1927).

¹⁰¹ Gowen, J. W., Murray, J. M., Gooch, M. E., and Ames, F. B., *Science*, **63**, 17 (1926).

¹⁰² Falkenheim, C., Vöitz, W., and Kirsch, W., *Klin. Wochschr.*, **5**, 2071 (1926), *Chem. Abs.*, **21**, 761 (1927).

¹⁰³ Hess, A. F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 636 (1926).

¹⁰⁴ Iguchi, K., and Mitamura, K., *J. Faculty Agr. Hokkaido Imp. Univ.*, **24**, Pt. 2, 39 (1928); *Chem. Abs.*, **23**, 2222 (1929).

¹⁰⁵ Büniger, H., *Zuchtungskunde*, **5**, 424 (1930); *Chem. Abs.*, **25**, 3409 (1931).

¹⁰⁶ Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, **22**, 1220 (1932).

by feeding the cow irradiated ergosterol.¹⁰⁷ The ergosterol need not, however, be isolated from the yeast before irradiation. Indeed, it has been stated that irradiated yeast is more effectively utilized.

The irradiation of dried yeast was described by Kirsch.¹⁰⁸ Previously, there had been patents for the treatment of various yeast extracts. Feher¹⁰⁹ boiled yeast with alkali, mixed it with organic solvents and separated and crystallized the upper phase. The recrystallized material was irradiated in thin layers and incorporated into cocoa butter and pressed into tablets. The Merck Co.¹¹⁰ proposed to treat only the non-saponifiable constituents of the yeast fat. MacLean¹¹¹ described an activated medical product obtained by incubating yeast in solutions containing phosphate and carbohydrate and subjecting the resulting sterols and fat to ultraviolet light. Autolyzed yeast has also been activated.¹¹²

The direct irradiation of layers of yeast about 0.1 inch thick at about a foot from a Hanovia burner was patented by Hall.¹¹³ Favorable reports on the irradiation of beer yeast with wave-lengths 2970 to 3020 Å were rendered by Schübel and Gehlen.¹¹⁴ According to Coward,¹¹⁵ exposure to strong sunlight suffices. The ability of irradiated yeast to protect young rats has been repeatedly demonstrated, and the material retains its potency for months or even years.¹¹⁶ Kon,¹¹⁷ however, noted a toxic effect to follow the prolonged administration of this material at a 1 per cent level, although Matzko¹¹⁸ did not observe this in the case of the use of customary amounts of a bakers' yeast irradiated to a potency of 5,000 to 10,000 units per gram.¹¹⁹

The daily administration of 500 I.U. of the vitamin in irradiated yeast during the five winter months to 69 normally growing infants protected them from moderate or marked rickets, and definite healing could also be effected within a month in marked rickets by this dose or its double.¹²⁰

The addition of irradiated yeast to the diet of cows was not found to alter either the assimilation of calcium and phosphorus or the quantity or quality of the milk by Hart, Steenbock, Kline and Humphrey.¹²¹ Kieferle¹²² agreed that there is no increase in the milk yield, but found an increase in its D content and a shortening of the lapse in the lactation period. The melting point of the milk fat was increased slightly and there was a slight decrease in the refractive index and in the Reichert-Meissl number. Others, however, have claimed to find an increase in the secretion of milk.¹²³ Kroon¹²⁴ found the increase as much as

¹⁰⁷ Thomas, B. H., and MacLeod, F. L., *Science*, **73**, 618 (1931). Gerstenberger, H. J., and Horech, A. J., [*J. Nutrition*, **5**, 479 (1932); *Chem. Abs.*, **26**, 5616 (1932)] found that milk from cows receiving large daily doses (200,000 rat units) was only mildly antirachitic, 9 quarts being slightly less active than a teaspoonful of cod-liver oil.

¹⁰⁸ Kirsch, W., *Biochem. Z.*, **196**, 294 (1928).

¹⁰⁹ Feher, G., *Hungarian P.* 100,696, Aug. 4, 1927; *Chem. Abs.*, **25**, 2524 (1931).

¹¹⁰ E. Merck Co., British P. 285,083, Feb. 9, 1928, *Chem. Abs.*, **22**, 4726 (1928); *Brit. Chem. Abs.*, **B**, 264 (1929).

¹¹¹ MacLean, I. S., British P. 295,757, May 23, 1927; *Brit. Chem. Abs.*, **B**, 797 (1928).

¹¹² Matsuoka, H., *Trans. Tottori Agr. Sci.*, **3**, 32 (1931); *Chem. Abs.*, **26**, 1645 (1932).

¹¹³ Hall, P., British P. 354,371, May 8, 1930, *Chem. Abs.*, **26**, 3870 (1932).

¹¹⁴ Schübel, K., and Gehlen, W., *Arch. Exptl. Path. Pharmacol.*, **166**, 348 (1932); *Chem. Abs.*, **26**, 5611 (1932).

¹¹⁵ Coward, K., *Lancet*, **II**, 920 (1933); *Chem. Abs.*, **28**, 509 (1934).

¹¹⁶ Vadimov, V., Voznava, A., and Semashko, V., *Elektrifikatsiya Sel'skogo Khozyaistva*, **2**, No. 8, 20 (1932); *Chem. Abs.*, **27**, 1032 (1933).

¹¹⁷ Kon, S. K., *Lancet*, **II**, 579 (1931); *Chem. Abs.*, **27**, 3242 (1933).

¹¹⁸ Matzko, S. N., *Arch. Tierernahrung Tierzucht.*, **9**, 623 (1933); *Chem. Abs.*, **28**, 6177 (1934).

¹¹⁹ Sveshnikova, N. P., *Trans. Dynamics of Development (U.S.S.R.)*, **9**, 311 (1935); *Chem. Abs.*, **30**, 3032-3 (1936).

¹²⁰ Drake, T., Tisdall, F. F., and Brown, A., *J. Nutrition*, **12**, 527 (1936); Drake, T., *Am. J. Diseases of Children*, **53**, 754 (1937). For Russian work on the value of various irradiated yeasts in poultry feeding, see Kratinova, E. P., and Pokhil, A. I., *Problems Animal Husbandry (U.S.S.R.)*, **1935**, No. 9, 93; *Chem. Abs.*, **30**, 2614 (1936); Zavadovskii, M., Lepskii, S., Kasheninikova, A., Samokhvalova, G., and Balezin, P., *Trans. Dynamics of Development (U.S.S.R.)*, **9**, 269 (1935); *Chem. Abs.*, **30**, 3032 (1936).

¹²¹ Hart, E. B., Steenbock, H., Kline, O. L., and Humphrey, G. C., *J. Biol. Chem.*, **86**, 145 (1930).

¹²² Kieferle, *Proc. World's Dairy Congr. Copenhagen*, Sect. I, 166, 1931; *Chem. Abs.*, **27**, 755 (1933).

¹²³ Bilek, F., and Hynek, L., *Zemrd Arch.*, **22**, 449 (1931); *Chem. Abs.*, **28**, 3447 (1934); Poelt, H., *Z. Vitaminforschung*, **1**, No. 4 (1932); *Chem. Abs.*, **28**, 1420 (1934).

¹²⁴ Kroon, H. M., *Milchwirtschaft Zentr.*, **60**, 325 (1932); *Chem. Abs.*, **26**, 3852 (1932).

25 to 30 per cent in the yield of milk as a result of feeding the yeast for three weeks after calving. Whatever may be true concerning the effect on the yield of milk, there have been many to show increases in the D potency when as much as 200 grams are fed daily.¹²⁵ Woelffer¹²⁶ found ten ounces of yeast of 30 D potency given daily to cows yielding thirty pounds of milk gave the milk a potency of 160 Steenbock units per quart. Yeast-fed cows require fifteen to twenty days to produce milk of the maximum potency, which is approximately 432 U.S.P. units per quart. High producers are more efficient than low producers in transferring the vitamin from the yeast to the milk. For efficient utilization, the yeast must be fed at least twice daily.¹²⁷

Higher potencies can be produced by feeding irradiated yeast than irradiated ergosterol as the source of the vitamin.¹²⁸ At about 180,000 units per cow per day, the potency of the yeast-milk may reach 150 to 160 rat units per quart, whereas that after feeding an equivalent number of units of irradiated ergosterol contains only 120 to 130. At lower feeding levels, however, the two sources are comparable in their results, but only a slight increase in the potency of the milk results. When the ergosterol fed was increased to 300,000 units, less than 2 per cent of the units ingested appeared in the milk.

There is little doubt that the method is a practical one for enriching the milk, but it is not as cheap as the direct irradiation of the milk. Spickard¹²⁹ believes irradiated milk with but 50 to 60 units per liter as effective as yeast-milk with 160 units per liter.

It is also possible to feed the cow irradiated dried molds. Thomas and Cannon¹³⁰ find that this has its greatest effect during the first few days of the feeding. After this, there is a rapid decline in the amount of the D secreted. In general, they believe the cow very inefficient in transferring added vitamin D from her diet to her milk. It is, of course, also possible to add concentrates from liver oils or other natural sources to the diet of the cow.

Such concentrates are, however, more commonly added to the milk to avoid the inefficiency of the transfer.¹³¹ Zucker¹³² adds a cod-liver oil concentrate in the proportion of one part in 12,000 of milk and obtains probably 150 units per quart, equivalent to about three teaspoons of cod-liver oil. Post¹³³ described concentrates by which milk may be fortified to 1500 U.S.P. units per quart. Some ergosterol irradiation products have occasionally been suggested.

Yeast-milk is particularly of value on the certified farm where the ration can be thoroughly controlled.¹³⁴ It is scarcely applicable to the general supply of cities which may require thousands of farms to meet their demand. For this purpose, direct irradiation of the milk is the most suitable method. By this method

¹²⁵ Lepsky, S., *Z. Zücht. B., Tierzücht.*, **26**, 237 (1933); *Chem. Abs.*, **27**, 2987 (1933); Golf, A., and Seeling, K., *Biedermann's Zentr. B., Tierernährung*, **6**, 65 (1934); *Chem. Abs.*, **28**, 2036 (1934); Schieblisch, M., *Biedermann's Zentr. B., Tierernährung*, **6**, 71 (1934); *Chem. Abs.*, **28**, 2036 (1934).

¹²⁶ Woelffer, E. A., *Cornell Veterinarian*, **23**, 313 (1933); *Chem. Abs.*, **28**, 3109 (1934); see also Smith, C. A., *Milk Plant Monthly*, **23**, No. 5, 24 (1934); *Chem. Abs.*, **28**, 4458 (1934).

¹²⁷ Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull.*, **173**, 52 (1935); *Chem. Abs.*, **29**, 5525 (1935).

¹²⁸ Russell, W. C., Wilcox, D. E., Waddell, J., and Wilson, L. T., *J. Dairy Sci.*, **17**, 445 (1934); *Chem. Abs.*, **28**, 5508 (1934).

¹²⁹ Spickard, V. W., *Northwest Med.*, **33**, 204 (1934); *Chem. Abs.*, **29**, 4465 (1935).

¹³⁰ Thomas, B. H., and Cannon, C. Y., *Iowa Agr. Exp. Sta. Report on Agr. Research*, **49** (1934); **26** (1933); *Chem. Abs.*, **29**, 3002, 3375 (1935).

¹³¹ Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull.*, **162**, 77 (1933); *Chem. Abs.*, **27**, 4563 (1933); Krauss, W. E., Bethke, R. M., and Wilder, W., *J. Dairy Sci.*, **16**, 549 (1933); Wyman, E. T., *New England J. Med.*, **209**, 889 (1933).

¹³² Zucker, T. F., *Am. J. Public Health*, **23**, 10 (1933).

¹³³ Post, C. I., *Milk Dealer*, **24**, No. 3, 39 (1934); *Chem. Abs.*, **29**, 4843 (1935).

¹³⁴ Hens, A. F., Lewis, J. M., MacLeod, F. L., and Thomas, B. H., *J. Am. Med. Assoc.*, **97**, 370 (1931).

the milk acquires a potency of about 135 U.S.P. units per quart. An outstanding advantage of the method is the reduction of the human element of error to a minimum by the development of irradiation equipment, mechanically controlled. It is also possible that the provitamin in milk is that which on irradiation yields a product more suited to the human than that from ergosterol. Hess¹³⁵ early showed the effectiveness of irradiated dried milk in infant feeding, as well as of irradiated yeast.

Another advantage of irradiating milk is the fact that it contains but a limited quantity of the provitamin so that too high a potency cannot be attained, thus avoiding any danger of an overdose.¹³⁶ Its use also requires no coöperation on the part of the mother and eliminates the giving of cod-liver oil.

In 1925, Steenbock, Hart, Hoppert and Black¹³⁷ found it possible to increase the antirachitic potency of cow milk more than eight times by exposing it to a quartz mercury arc. That of goat milk could be increased twenty-four times. Milk irradiated on a large scale by the methods of Supplee and Dorcas has been extensively studied in the laboratory and clinic by Hess and Lewis¹³⁸ who find it a highly effective and reliable antirachitic agent. A quart or even less of the milk daily sufficed to protect infants from rickets, although this amount contained only 50 units as assayed by a standard rat method. The full explanation as to why smaller numbers of rat units are adequate when given in this form than in cod-liver oil has not yet been given. That it might be more effective than an equivalent number of rat units of irradiated ergosterol could be accounted for by a difference in the structures of the vitamins, the human differentiating between these although the rat does not. But presumably the natural vitamin in cod-liver oil is the same as that of milk so that the doses from the two sources which are equally effective on the rat should also be equally effective on the human. This assumption has, however, not yet been proved and it must remain an assumption until the vitamin has been isolated from irradiated milk and compared chemically with D₈. Other suggestions for the discrepancy may be offered. It may be related to the presence of other substances in the milk and in the cod-liver oil which alter the ease of absorption of the vitamin.¹³⁹ Supplee, Ansbacher, Bender and Flanigan¹⁴⁰ attribute the unexpected effectiveness of irradiated milk to the formation of a "symplex system" between the vitamin and a colloidal carrier such as lactalbumin. This they believe can form only in lipid-free lactalbumin. When lipids are present, the vitamin merely dissolves in the prosthetic group or lipid associated with the lactalbumin. This they suggest accounts also for the observation of Lewis¹⁴¹ that vitamin D administered in the water phase with propylene glycol with accompanying milk constituents is more effective than when it is carried by an oil vehicle. Ansbacher and Supplee had found that about 18 per cent of the total milk cholesterol is associ-

¹³⁵ Hess, A. F., *J. Am. Med. Assoc.*, **89**, 337 (1927); see also Eddy, W. H., *Arch. Pediat.*, **44**, 320 (1927); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **34**, 364 (1927); *J. Biol. Chem.*, **75**, 227 (1927); **73**, 617 (1927).

¹³⁶ Mohr, W., Kulteren, S., and Richter, V., *Molkerei-Z., Hildesheim*, **45**, 545 (1931); *Chem. Abs.*, **26**, 3010 (1932).

¹³⁷ Steenbock, H., Hart, E. B., Hoppert, C. A., and Black, A., *J. Biol. Chem.*, **66**, 441 (1925).

¹³⁸ Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, 647 (1932). An early German product—Hanauer milk—had an activity such that 100 cc. corresponded to 5-6 gram of commercial cod-liver oil. Bamberger, P., *Deut. med. Wochschr.*, **55**, 1547 (1929); *Brit. Chem. Abs.*, **B**, 637 (1930).

¹³⁹ For evidence of the disparity of doses see, Hess, A. F., Lewis, J. M., McLeod, F. L., and Thomas, B. H., *J. Am. Med. Assoc.*, **97**, 370 (1931); Wyman, E. T., and Butler, A. M., *Am. J. Diseases of Children*, **43**, 1509 (1932); Gerstenberger, H., and Horsh, A., *J. Nutrition*, **5**, 479 (1932); Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, 647 (1932); **101**, 181 (1933).

¹⁴⁰ Supplee, G. C., Ansbacher, S., Bender, R. C., and Flanigan, G. E., *J. Biol. Chem.*, **114**, 95 (1936); Ansbacher, S., and Supplee, G. C., *J. Biol. Chem.*, **105**, 391 (1934).

¹⁴¹ Lewis, J. M., *J. Pediatrics*, **6**, 362 (1935).

ated with proteins, chiefly lactalbumin. It is to this prosthetically bound, cholesterol-like lipid, rather than to that free in the butter-fat, that they attribute the ability to form, on irradiation, a particularly effective antirachitic agent.

Before describing the methods employed by Supplee and others, brief mention will be made of the difficulties which must be overcome and of some of the methods proposed in Germany and elsewhere. The early attempts to irradiate milk were usually marked by a tendency to overirradiate it with resultant deterioration in odor and taste. Schultz¹⁴² attributed this to the action of hydrogen peroxide upon the protein and found that this change did not parallel the production of the antirachitic potency. The irradiation of the cream alone did not affect the taste. He claimed that 15 grams of irradiated protein-free milk-fat cured rickets in children.¹⁴³ As yet, however, relatively little is known as to the nature of the deterioration due to overirradiation. Energy between 2600 and 3100A appears less active in flavor production than that of wave-lengths shorter than 2600A. The range from 3100 to 3800A is more active in causing flavor changes than that from 3800 to 7000A.¹⁴⁴

Anderson and Triebold¹⁴⁵ passed milk through a commercial irradiator eight times and could detect no marked changes in the chemical composition or in the fat constants. Although the induction period for the oxidation of the fat was reduced from twenty to seventeen hours by irradiation, the rate of deterioration over a period of six months was unchanged. Digestion studies *in vitro* with pepsin and with trypsin indicated a slightly increased rate in the early stages due possibly to the destruction of an antienzyme. Hoffman¹⁴⁶ used a mercury-argon discharge tube which emits little heat radiation¹⁴⁷ in the effort to lessen the changes in taste. To overcome the difficulty of a lack of penetration of the milk by the effective rays (not over 0.1 mm.), he arranged to have it flow through an adjustable slotted distributor onto a cylindrical net of narrow-mesh wire in the center of which was placed the source. For treating raw milk, he conducted the process in the presence of an inert gas to avoid the destructive action of ozone on vitamins A and C.

Commercial milk irradiation appears to have been first carried out in Germany. It is not feasible to give the details of the apparatus there suggested.¹⁴⁸

The Dry Milk Co.¹⁴⁹ proposed to spray the milk (liquid or powdered) before the source for a period as short as eight seconds which, with the intensities used, permitted the development of 75 per cent of the possible antirachitic potency before the formation of a disagreeable odor or taste. Most irradiate the milk in thin flowing films.¹⁵⁰

Salmony-Karsten¹⁵¹ believed it necessary to use an inert gas to exclude oxygen

¹⁴² Schultz, O., *Milchw. Forsch.*, **4**, 37 (1927); *Chem. Abs.*, **21**, 3631 (1927).

¹⁴³ Schultz, O., *Klin. Wochschr.*, **6**, 848 (1927); Schultz, O., and Rohr F., *Deut. med. Wochschr.*, **33**, 1255 (1927).

¹⁴⁴ Weckel, K. G., Jackson, H. C., Haman, R., and Steenbock, H., *Ind. Eng. Chem.*, **28**, 653 (1936).

¹⁴⁵ Anderson, A. K., and Triebold, H. O., *J. Dairy Sci.*, **15**, 469 (1932); *Chem. Abs.*, **27**, 784 (1933).

¹⁴⁶ Hoffman, *Proc. 8th World Dairy Conference*, 460 (1928); *Chem. Abs.*, **23**, 5491 (1929).

¹⁴⁷ From, V. C., Rowley, C. D., and Larsky, A. W., *British P.* 346,682, Oct. 15, 1929, *Chem. Abs.*, **26**, 537 (1932) specify the simultaneous use of infrared rays.

¹⁴⁸ Geffcken, H. H., and Richter, H., *German P.* 557,334, March 19, 1927; 545,080, March 19, 1927; 545,886, Jan. 3, 1928, Löwenstein, L., *German P.* 552,263, June 6, 1928, *Chem. Abs.*, **27**, 353 (1933); Schindler, A., *German P.* 572,491, Feb. 8, 1927; Wiegand, K., *German P.* 541,991, Oct. 30, 1927; 553,016, Dec. 21, 1927; Ried, O., *Austrian P.* 116,463, Sept. 15, 1929; *Chem. Abs.*, **24**, 2837 (1930); Kirsch, W., *Chem. Fabrik*, 150 (1928).

¹⁴⁹ *British P.* 298,585, June 11, 1927, to Dry Milk Co.; *Brit. Chem. Abs.*, **B**, 911 (1928).

¹⁵⁰ Trebler, H. A., U. S. P. 2,001,555; *British P.* 428,434, May 13, 1935. In this a single unit irradiates several flowing sheets of milk. Trebler, H. A., and Larsen, C. J., U. S. P. 2,018,332; *British P.* 432,011, July 18, 1935; see also Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395; Cuny, L., *British P.* 441,524, Jan. 21, 1936; Berndt, E. C., and Creighton, H. M., U. S. P. 2,065,054-5, *Chem. Abs.*, **31**, 773, 2701 (1937); Henszey, R. O., U. S. P. 2,060,865, *Chem. Abs.*, **31**, 1665 (1937).

¹⁵¹ Salmony-Karsten, A., *Chimie et industrie*, **22**, 259 (1929); Chesney, J., U. S. P. 1,723,603, Aug. 6, 1929; *Chem. Abs.*, **23**, 4512 (1929) also excluded air.

and also to add a means for cooling the milk during the process. Hickman and Hickman¹⁵² pointed out that exclusion of air is unnecessary when the milk is exposed while flowing in a thin film on one side of a milk cooler. The irradiation is for a period of 8 to 30 seconds at a distance of 11 inches from a 2000 c.p. quartz mercury-vapor lamp with reflectors.

Since it is a lipid that is the provitamin, the question has been raised as to whether it might not be better to irradiate the cream separately. Essig¹⁵³ found irradiated skimmed milk to be only slightly protective, although the same whole milk when irradiated was highly effective. Kersten and Schultz¹⁵⁴ irradiate the cream and then return it to the milk from which it had been separated. Recently, however, Supplee gave reasons for believing that the effectiveness depends in some manner upon an association of the vitamin with lactalbumin, so that the separation of the cream seems unnecessary. Furthermore, Dorcas and Supplee¹⁵⁵ find that under given irradiation conditions, the potencies which can be attained are not in proportion to the amount of fat present. Relatively high potencies are shown in samples with low amounts of fat. Krauss, Bethke and Washburn,¹⁵⁶ find, however, that as the fat percentage increases, the activatability is also increased. Still the solids-not-fat fraction of Holstein milk may contain more of the provitamin than that of Jersey milk, since the two milks can be activated to the same extent even though the Jersey milk contains more fat and has a higher original potency.

Hoefelmayer¹⁵⁷ described the irradiation of condensed, dried or curdled milk. Favorable results of clinical studies on the use of irradiated powdered whole milk were reported by De Sanctis, Ashton and Stringfield.¹⁵⁸ Weckel and Jackson¹⁵⁹ believed the most feasible method of irradiating milk was after evaporation of raw standardized milk at 208-210°F. until it contained 7.8 to 8.3 per cent of fat. The hot milk from the vacuum pan was then irradiated by a carbon arc by passage over a conical irradiator, after which it was homogenized, canned and sterilized. When diluted to the solid content of normal milk, the vitamin potency was 50 Steenbock units per quart, corresponding to 135 U.S.P. units. Cream could be successfully irradiated without the formation of undesirable flavors or chemical deterioration. Acids developed somewhat more slowly in irradiated than in untreated milk. Supplee, Bender, Flanigan, Dorcas and Greider¹⁶⁰ find, however, that the irradiation of evaporated milk does not result in as high a degree of potency as the irradiation of fluid milk when films of the same capacity* are subjected to the same intensity and quality of ultraviolet radiations. Since the films of the same capacity of evaporated milk are thicker and more dense than those of fluid milk, the penetration is correspondingly less. Greater antirachitic potency of evaporated milk may be attained by the exposure of thinner films for longer periods of time or by increasing the intensity of the source, but it still does not equal that attainable by

¹⁵² Hickman, J. O., and Hickman, N. V., British P. 325,470, Sept. 12, 1928; *Brit. Chem. Abs.*, **B**, 484 (1930). See also Bragg, J. H., U. S. P. 1,954,065, April 10, 1934; *Chem. Abs.*, **28**, 3807 (1934).

¹⁵³ Essig, B., *Munch. med. Wochschr.*, **78**, 273 (1931); *Chem. Abs.*, **25**, 4924 (1931).

¹⁵⁴ Kersten, G., and Schultz, O., German P. 577,531, June 1, 1933; *Chem. Abs.*, **28**, 541 (1934).

¹⁵⁵ Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).

¹⁵⁶ Krauss, W. F., Bethke, R. M., and Washburn, R. G., *J. Dairy Sci.*, **19**, 739 (1936).

¹⁵⁷ Hoefelmayer, K., British P. 265,910, Feb. 12, 1926; *Chem. Abs.*, **22**, 468 (1928).

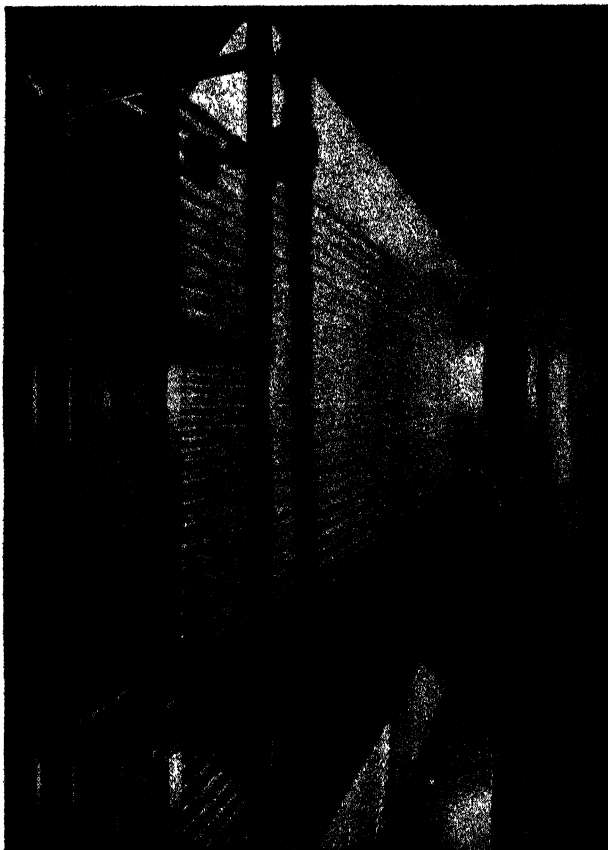
¹⁵⁸ De Sanctis, A. G., Ashton, L. O., and Stringfield, O. L., *Arch. Pediatr.*, **46**, 297 (1929); *Chem. Abs.*, **23**, 3956 (1929).

¹⁵⁹ Weckel, K. G., and Jackson, H. C., *Natl. Butter and Cheese J.*, **25**, No. 11, 24 (1934); *Chem. Abs.*, **28**, 5857 (1934); *Wisconsin Agr. Exp. Sta., Bull.* 428, 33 (1934); *Chem. Abs.*, **29**, 3052 (1935).

¹⁶⁰ Supplee, G. C., Bender, R. C., Flanigan, G. E., Dorcas, M. J., and Greider, C. E., *J. Dairy Sci.*, **19**, 67 (1936).

* The capacity is the film thickness times the distance of film travel.

the irradiation of fluid milk films. The degree of activation imparted to evaporated milk is not significantly different when homogenized and non-homogenized products are irradiated nor is it affected by varying the temperature between 55 and 165°F. The ultraviolet transmission is progressively decreased by preheating to 180°F., by concentration and by homogenization, as a result of physical changes in the inherent milk constituents.



Courtesy National Carbon Co., Inc.

FIGURE 156. Flat Type Milk Irradiating Unit.

From an engineering point of view the process has been studied most thoroughly by Supplee and co-workers. The most significant feature which has emerged under commercial conditions (treatment of 1000 lb. lots) is that the time of irradiation by either a quartz mercury-vapor lamp or a carbon arc need be but a few seconds, obviating changes in taste.¹⁶¹

The milk in 1000 lb. lots was exposed as a moving film (0.4 mm.) which received the rays at constantly changing angles of incidence varying from 0 to 90°. The

¹⁶¹ Supplee, G. C., and Dorcas, M. J., *Lait*, 14, 1, 125 (1934); *Chem. Abs.*, 28, 3143 (1934); Supplee, G. C., U. S. P. 1,817,936, Aug. 11, 1931 (to Borden Co.); *Chem. Abs.*, 25, 5477 (1931); Supplee, G. C., Dorcas, M. J., and Hess, A. F., *J. Biol. Chem.*, 94, 749 (1932)

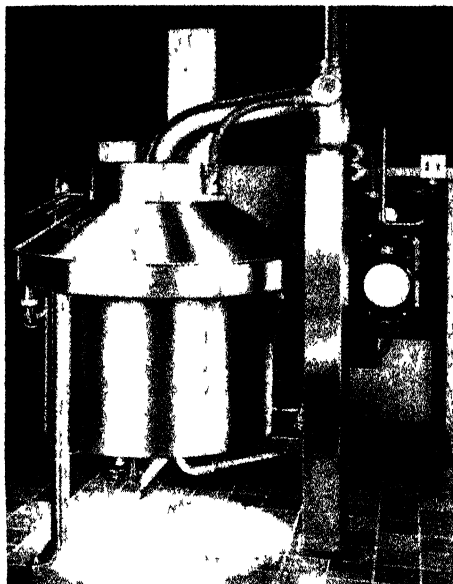
complete cycle of exposure to the range of impingement angles required a period of about 0.3 second. The maximum potency was found to be attained within the first few seconds. Over 238 variations in the irradiation conditions were studied in this investigation.

There are two main types of apparatus which are employed in conjunction with the carbon arc, the flat and drum types (Figures 156 and 157). Units of various capacities have been employed. The capacity may be as low as 625 quarts per hour, and from these larger synchronized units may be assembled. A unit employed early by the Dryco Co.¹⁶² had a normal capacity for the treatment of more than 5000 quarts per hour.

FIGURE 157.

National Type YN Milk
Irradiating Unit

Courtesy National Carbon Co., Inc.



Supplee, Beck and Dorcas,¹⁶³ by comparing the quanta of energy applied per cc. with the molecules of vitamin D formed per cc. showed that the potency is dependent upon the amount of energy applied, provided that the radiations lie within the antirachitic range. It was immaterial whether the energy was from the Corex D filtered or unfiltered carbon arc or consisted of reflected rays only. This was true within the limits of energy of 409×10^3 ergs (545×10^{14} quanta) and 9486×10^3 ergs ($12,480 \times 10^{14}$ quanta). Mica screens which transmit practically no energy below 2900A and only 45 per cent at 3150A do not permit any source to increase the potency of the milk. The relative effectiveness of an equivalent amount of energy from different sources was in the following order: C carbon, Mg carbon, mercury arc and Sunshine carbon. When time and intensity were taken into account for practical purposes the effectiveness of the sources tested increased in the order: Mercury-vapor arc, Sunshine carbon arc, magnesium carbon arc and

¹⁶² Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, 22, 1220 (1932).

¹⁶³ Supplee, G. C., Beck, H. H., and Dorcas, M. J., *J. Biol. Chem.*, 98, 769 (1932).

C carbon arc. The use of Corex D filters reduces the amount of energy reaching the milk per unit of time and causes a commensurate reduction in the rate of building up the potency. The effects of chromium-plated reflectors on the energy incident at normal incidence on milk at 61 cm. from an arc have been computed by Supplee, Hanford, Dorcas and Beck,¹⁶⁴ for the wave-length ranges 2,000-2,200A, 2,200-2,400A and 2,400-3,000A.

It was found by biological assays that the total quanta which must be applied to produce a plus-one line test in the rachitic rat was 5949×10^{15} . From the quantity of irradiated milk required and the assumptions that this must be equivalent to 0.03% of D₂ and that its molecular weight is that of ergosterol, it was concluded that there had been produced 4.5×10^{13} molecules of the vitamin. (This implies that during the first few seconds when a definite amount of energy produces a definite amount of vitamin, the quantum yield is low, about 7×10^{-6} . Compare with the high quantum yields reported for the irradiation of ergosterol solutions, chapter 39. Evidently much of the energy is absorbed by other constituents of the milk). When the incident energy is increased beyond a certain point, $2,000-3,000 \times 10^{14}$ quanta per cc., little or no additional formation of vitamin occurs or destruction begins within very brief periods. The maximum concentration was reached after a total of about 2.5 million ergs per cc. had been applied. The concentration is then about 2.5% per liter or practically twelve times that of the untreated milk.

The reflection of ultraviolet rays from the surface of milk is of the same order of magnitude as that from a water surface.¹⁶⁵ The degree of reflection increases as the angle of incidence decreases. At 75° and 45° incidence, about 3 per cent of the energy between 2550 and 3000A is reflected. At 30°, it is about 6 per cent, at 20° 13.4 per cent, 15° 28 per cent and from a 10° angle about 34 per cent. Milk films show selective reflection throughout the range of wave-lengths 2550 to 3300A, most pronounced at angles of incidence of 30° or less.

Only 20 to 40 per cent of the energy between 2500 and 2850A striking the surface of a milk film at right angles on a smooth quartz flowboard are transmitted by films 0.02 mm. thick.¹⁶⁶

Films 0.11 mm. thick transmit 5 per cent or less of the incident energy within these limits. As the fat content of the milk is increased, the transmission is somewhat decreased. The transmission increases rapidly and progressively in the longer wave length region 2800 to 3300A.

Under suitable conditions of high intensity, a high degree of activation can be obtained from exposures varying from less than a second to not more than two seconds. It is probable that the reaction occurs chiefly at the moving surface since extremely thin but slow-moving films showed a lower degree of activation after momentary exposure than did thicker but faster-moving ones. With high intensities it is also possible to produce measurable antirachitic properties in milk derivatives containing little or no butter fat.¹⁶⁷ Studies on the influence of various changes in film capacity, (that is film thickness \times the distance of film travel), have also been reported.¹⁶⁸

Whole milk irradiation units are made by the Cherry-Burrell Corporation, the Creamery Package Manufacturing Co.¹⁶⁹ and the Hanovia Co. (Figures 158 and 159).

¹⁶⁴ Supplee, G. C., Hanford, Z. M., Dorcas, M. J., and Beck, H. H., *J. Biol. Chem.*, **95**, 687 (1932).

¹⁶⁵ Supplee, G. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 607 (1934).

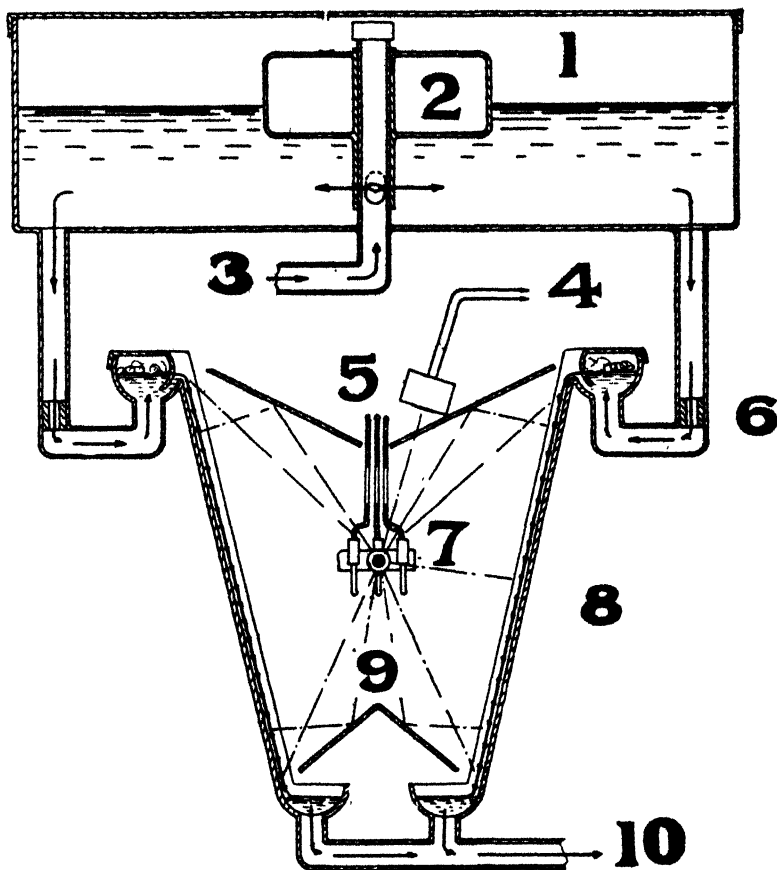
¹⁶⁶ Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).

¹⁶⁷ Supplee, G. C., Flanigan, G. E., Bender, R. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 483 (1934).

¹⁶⁸ Supplee, G. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 527 (1934).

¹⁶⁹ British P. 450,341, July 15, 1936, to Creamery Package Manufacturing Co.

In these,¹⁷⁰ the milk is exposed while flowing on nearly vertical metal surfaces in thin films of about 300 to 350 lbs. per horizontal linear foot per hour. The effective distances traversed during exposure range from 9 to 60 inches in different types of equipment, using various sources and operating intensities. By means of a reflected light beam method, Beck and Weckel¹⁷¹ determined the thickness at various horizontal levels of milk flowing by gravity in films of various capacities (lbs. per linear foot per hour) over vertical steel surfaces. At 200 lbs. per foot per hour or less, the films



Courtesy of the Hanovia Co.

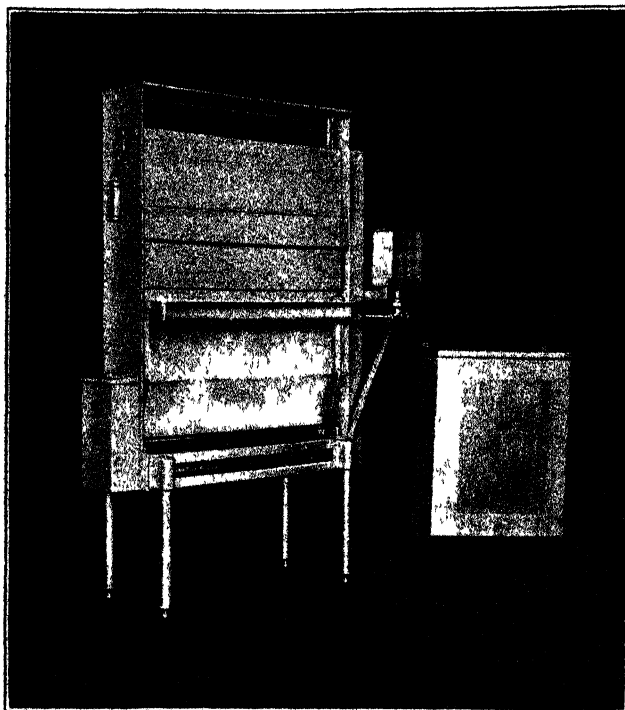
FIGURE 158. Diagram of Hanovia Milk Irradiator.

are of uniform thickness throughout their course of flow. At 300 lbs. per foot per hour, the thickness is variably greater in the first two or three inches of travel, but then becomes uniform. Under these conditions, the motion is accelerated at a decreasing rate in the first two or three inches, after which the flow attains a steady rate. For practical purposes, the average time for films of various capacities to traverse given distances is directly proportional to the distance traversed. A direct proportion between travel time and D potency was established. This may be due to the fact that the flow is turbulent, causing an interchange of substances in the surface zone within which

¹⁷⁰ Beck, H. H., and Weckel, K. G., *Ind. Eng. Chem.*, **28**, 1251 (1936).

¹⁷¹ Beck, H. H., and Weckel, K. G., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 258 (1936). See also Beck, H. H., Jackson, H. C., and Weckel, K. G., *Ind. Eng. Chem.*, **30**, 632 (1938).

the absorption and reaction occurs. The thickness of the film in thousandths of an inch may be calculated from the capacity X by the expression: $T=1.79 X^{0.875}$. The average velocity in inches per second is given by $0.349 X^{0.685}$. The potency has a parabolic relation to the amount of active radiation applied, and the film capacity-potency relation is hyperbolic. O'Brien, McEwen and Morgareidge¹⁷² calculate that if all the provitamin in whole milk could be converted, the potency would be 2.0 I.U. per gram. Using arc inputs of 300 joules per gram, they obtained 1.65 I.U. per gram.



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 159. Hanovia Milk Irradiator.

During the commercial irradiation of milk, the destruction of vitamin A is insignificant or not measurable,¹⁷³ but vitamin C may be slightly affected, although to an extent less than the usual variations in non-irradiated milk.¹⁷⁴

The question has often been raised as to whether better prophylactic results can be obtained by irradiation than by the administration of the vitamin in some form. Apparently, there is little if any difference, but since radiation therapy is less readily available the latter must usually be relied upon in practice.¹⁷⁵

¹⁷² O'Brien, B., McEwen, H. D., and Morgareidge, K., *Ind. Eng. Chem.*, 30, 839 (1938).

¹⁷³ Supplee, G. C., and Dow, O. D., *J. Biol. Chem.*, 75, 227 (1927); *Am. J. Diseases of Children*, 41, 1353 (1931); Cannon, H. J., and Hixson, O. F., *Ind Eng Chem*, 28, 1009 (1936)

¹⁷⁴ See also Schoenleber, F. C., Steenlock, H., and Baumann, C. A., *Wis. Agr. Expt. Sta. Bull.* 435, 66 (1936); *Chem. Abs.*, 32, 2986 (1938).

¹⁷⁵ British Med. Research Council, *J. Soc. Chem Ind*, 48, 279 (1929), Gorter, E., and Soer, J. J., *Nederland. Tijdschr. Geneesk.*, 74, II, 4310 (1930); Machti, A., *Pediatria Rivista*, 37, 1175 (1929); Shohl, A. T., and Bing, F. C., *Am J. Physiol.*, 86, 633 (1928); von Noel, L., and Dannmeyer, F., *Strahlentherapie*, 32, 769 (1929); *Chem. Abs.*, 24, 4808 (1930); Blunt, K., and Cowen, R., "Ultra-violet Light and Vitamin D. in Nutrition," Univ. of Chicago Press, 1930.

It has been demonstrated by Hume, Lucas and Smith¹⁷⁶ that vitamin D from irradiated cholesterol can be absorbed from a small area of undamaged skin in amounts sufficient to supply the needs of the rat and rabbit. Similar results have been recorded by Astrowe and Morgen,¹⁷⁷ by Fodor,¹⁷⁸ by Amrhein,¹⁷⁹ and by Helmer and Jansen.¹⁸⁰

The demonstration that the vitamin is absorbed from the skin and the assumption that it may exert a beneficial effect on the skin have prompted many proposals for its local application. Lorenz and Wodlinger¹⁸¹ incorporate an irradiated sterol in toilet soap during crutching or milling. Cholesterol, phytosterol, zymosterol, etc. were irradiated with x-rays, infrared rays or cathode rays. Wearham¹⁸² adds ergosterol to the soap or to the fats to be saponified and irradiates the mixture.

In a cosmetic skin cream, Goodall¹⁸³ proposed the use of cottonseed oil which had been treated with ultraviolet rays along with a mineral oil and a waxy substance. Apparatus for irradiating wool fat or wool-fat alcohols for use in cosmetic creams has been described.¹⁸⁴

Autolyzed yeast, mixed with organic solvents and irradiated, has been proposed for use in treating the skin.¹⁸⁵

¹⁷⁶ Hume, F. M., Lucas, N. S., and Smith, H. H., *Biochem. J.*, **21**, 362 (1927).

¹⁷⁷ Astrowe, P. S., and Morgen, R. A., *Am. J. Diseases Children*, **49**, 912 (1935); *Chem. Abs.*, **29**, 5158 (1935).

¹⁷⁸ Fodor, M. E., *Z. Vitaminforschung*, **3**, 241 (1934); *Chem. Abs.*, **29**, 5487 (1935).

¹⁷⁹ Amrhein, F. J., *J. Am. Pharm. Assoc.*, **22**, 182 (1934); *Chem. Abs.*, **28**, 5505 (1934). For a review, see Schuler, R., *Drug and Cosmetic Industry*, **38**, 485 (1936).

¹⁸⁰ Helmer, A. C., and Jansen, C. H., *Studies Inst. Divi Thomae*, **1**, 83, 99 (1937).

¹⁸¹ Lorenz, A. J., and Wodlinger, M. H., *British P.* 403,083, June 10, 1932; *Chem. Abs.*, **28**, 3261 (1934); *French P.* 742,181, March 1, 1933; *Chem. Abs.*, **27**, 3632 (1933); Lorenz, A. J., *U. S. P.* 2,060,228 (to Lever Bros.); *Chem. Abs.*, **31**, 566 (1937).

¹⁸² Wearham, J., *British P.* 403,650, Dec. 20, 1933; *Chem. Abs.*, **28**, 3261 (1934).

¹⁸³ Goodall, F. E., *U. S. P.* 1,636,814, May 3, 1927; *Chem. Abs.*, **21**, 2171 (1927).

¹⁸⁴ Leo-Werke, *German P.* 622,373, Nov. 27, 1935; *Austrian P.* 137,455, May 11, 1934.

¹⁸⁵ Baeder Illatszergyar, R. T., *Hungarian P.* 114,585; July 1, 1936; *Chem. Abs.*, **30**, 7284 (1936).

Chapter 41

Ultraviolet Light and Other Vitamins

Although some have suggested that vitamins other than D may also be produced by the irradiation of precursors,¹ no evidence exists for such processes. Suggestions have been made repeatedly that the formation of vitamins, particularly A and C, is in some manner related to the processes of photosynthesis.²

Too little is yet known of the mechanism of the photosynthetic formation of carbohydrates for definite statements to be made regarding a possible participation of either vitamin A or C, but the evidence as yet available is not very strongly in favor of this viewpoint.

Measurements of the ultraviolet absorption spectra of vitamin concentrates have significantly aided in the isolation and identification of the vitamins, and studies of the destruction of the purified compounds during irradiation have led to definite results.

Vitamin C. Reyher and Meller³ observed that a prolonged irradiation of milk with exclusion of air causes some loss in its antiscorbutic properties. When irradiated in an open vessel under conditions in which ozone may be formed, there is a complete destruction of the vitamin. The loss which occurs in the practical irradiation of milk for the production of vitamin D is not important.⁴ Booth and Kon⁵ observed that milk which originally gave the vitamin C test based upon the reduction of the indophenol reagent, failed to do so after direct exposure to sunlight. Treatment for an hour with hydrogen sulfide restored 90 per cent of the original reducing value. The non-restorable loss increased with the duration of the exposure, so that after six hours only 50 per cent could be restored by the hydrogen sulfide treatment. The destruction follows a unimolecular course. The destruction in milk may be photosensitized by lactoflavin.⁶ Indeed, Hopkins maintains that in pure buffered solutions at pH 7.4, ascorbic acid is stable in sunlight, although it is rapidly oxidized in the presence of small amounts of lactoflavin.⁷ Ultraviolet light, however, causes a decomposition of *l*-ascorbic acid, even in the absence of oxygen.⁸ This change is also accelerated by lactoflavin, but is retarded by acid. Dehydroascorbic acid could not be detected in the products formed. This oxidized form is not affected by irradiation.

Milanesi⁹ failed in attempts to increase the amount of this vitamin in oats by irradiation and concluded that it was destroyed or altered by the treatment.

¹ Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932).

² Heller, V. G., and St. Julian, R. R., *J. Nutrition*, **4**, 227 (1931); *Chem. Abs.*, **25**, 5915 (1931); Heller, V. G., *J. Biol. Chem.*, **76**, 499 (1928); Crist, J. W., and Dye, M., *Ibid.*, **91**, 127 (1931); Smith, L. L. W., and Morgan, A. F., *Ibid.*, **101**, 43 (1933).

³ Reyher, P., and Meller, B., *Klin. Wochschr.*, **5**, 2341 (1926); *Chem. Abs.*, **21**, 2149 (1927).

⁴ Hottinger, A., *Klin. Wochschr.*, **6**, 1793 (1927); *Chem. Abs.*, **22**, 798 (1928); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **41**, 1353 (1931).

⁵ Booth, R. G., and Kon, S. K., *Nature*, **134**, 936 (1934); Kon, S. K., and Watson, M. B., *Biochem. J.*, **30**, 2273 (1936).

⁶ Hand, D. B., Guthrie, E. S., and Sharp, P. F., *Science*, **87**, 439 (1938).

⁷ Hopkins, F. G., *Compt. rend. trav. lab. Carlsberg, Sér. chim.*, **22**, 226 (1938); *Chem. Abs.*, **32**, 6265 (1938).

⁸ Kellie, A. E., and Zilva, S. S., *Biochem. J.*, **32**, 1561 (1938).

⁹ Milanesi, E., *Boll. soc. ital. biol. sper.*, **3**, 240 (1928); *Chem. Abs.*, **22**, 3911 (1928).

Cultrera¹⁰ found the reducing factor of lemon juice to be destroyed by Wood's light. According to v. Euler and Klusmann,¹¹ the optical activity of hexuronic acid decreases when it is kept in a current of oxygen under ultraviolet rays. Ascorbic acid is now known to have an absorption maximum at 2600Å in water and at 2630 to 2650Å in alcohol.¹²

Eggleton and Harris¹³ conclude that light is unnecessary for the natural synthesis of this vitamin. Irradiation of infant food did not increase its content of ascorbic acid. Mercury-arc irradiation of cabbage in which the vitamin had been destroyed by heat gave but a doubtful regeneration. Irradiation has no curative action on scorbutic animals.¹⁴ Heller¹⁵ has claimed that the formation of vitamin C (and also A), although it occurs during the germination and early growth of seedlings in darkness, is accelerated by exposure to light. Similar observations have since been reported by Matsuoka¹⁶ and by Lee and Read.¹⁷ Virtanen and Eerola¹⁸ tend to ascribe such results to an effect of temperature rather than light, at least in the case of the pea.

It has been claimed that a brief irradiation by ultraviolet light of the skin of a guinea pig increases its ascorbic acid content, although a longer one (25 minutes) decreases it.¹⁹

The claim of Rygh²⁰ that vitamin C could be obtained by the irradiation of narcotine derivatives has since been refuted.²¹ It appears to have been based upon unsuitable biological testing of the irradiation product.

Several observers have noted irradiation, particularly with visible light in the presence of a photosensitizer such as methylene blue, to lower the redox potential of ascorbic acid.²² It has been proposed to take advantage of this property in a method for the assay of ascorbic acid in tissues.²³ Cornbleet²⁴ finds irradiation of skin to lower its ascorbic acid content. Pigmented skin has more ascorbic acid than fair skin. Buruiană believes it possible to determine the vitamin C content of milk by comparing the reduction of iodine before and after the exposure of the milk to sunlight.²⁵

¹⁰ Cultrera, R., *Ind. ital. conserve aliment.*, **9**, 9 (1934); *Chem. Abs.*, **28**, 3763 (1934).

¹¹ v. Euler, H., and Klusmann, E., *Svensk Kem. Tid.*, **44**, 290 (1932); *Chem. Abs.*, **27**, 4566 (1933).

¹² Herbert, R. W., and Hirst, E. L., *Nature*, **130**, 205 (1932); *Biochem. J.*, **29**, 1881 (1935); Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932); Karret, P., Schwarzenbach, G., and Schopp, K., *Helv. Chim. Acta*, **16**, 181 (1933); Robertson, E. B., *J. Soc. Chem. Ind.*, **53**, 277 (1934); Plaut, F., Bulow, M., and Pruckner, F., *Z. physiol. Chem.*, **234**, 131 (1935).

¹³ Eggleton, P., and Harris, L. J., *Brit. Med. J.*, **II**, 989 (1925); *Chem. Abs.*, **20**, 1651 (1926).

¹⁴ Holtz, P., and Wölpert, K., [*Arch. Exptl. Path. Pharmacol.*, **182**, 164 (1936)] believed it to cause some delay in the onset of scurvy.

¹⁵ Heller, V. G., *J. Biol. Chem.*, **76**, 499 (1928).

¹⁶ Matsuoka, T., *Mem. Coll. Agr. Kyoto Imp. Univ.*, **24**, 37 (1932); **35**, 93 (1935); *Chem. Abs.*, **27**, 2180 (1933); **30**, 139 (1936); *J. Agr. Chem. Soc. Japan*, **9**, 81 (1933); **12**, 1203 (1936); *Chem. Abs.*, **31**, 3103 (1937).

¹⁷ Lee, Wei-Yung, and Read, B. E., *J. Chinese Chem. Soc.*, **4**, 208 (1936); *Chem. Abs.*, **31**, 430 (1937). See also Tsuge, H., and Kurihara, K., *Sei-i-kai Med. J.*, **56**, No. 6, 894 (1937); *Chem. Abs.*, **31**, 8610 (1937); Randon, L., Giroud, A., and Katsimamanga, R., *Compt. rend. soc. biol.*, **126**, 1068 (1937); *Chem. Abs.*, **32**, 2570 (1938).

¹⁸ Virtanen, A. I., and Eerola, L. V., *Suomen Kemistilehti*, **9B**, 13 (1936); *Chem. Abs.*, **31**, 2254 (1937). See, however, Veselkin, N. V., Lyubimenko, V. N., Bulgakova, S. P., Tchal'skaya, V. V., and Engel, I. S., *Izv. Nauch. Inst. Lesgafita*, **17**, 389, 405 (1934); *Chem. Abs.*, **31**, 6096 (1937).

¹⁹ Castellini, P., *Gior. ital. dermatol. sifilol.*, **77**, 967 (1936); *Chem. Abs.*, **32**, 226 (1938).

²⁰ Rygh, O., Rygh, A., and Laland, P., *Z. physiol. Chem.*, **204**, 105; **211**, 275 (1932).

²¹ Westin, G., *Z. Vitaminforsch.*, **2**, 1 (1933); *Chem. Abs.*, **27**, 4560 (1933); Shimada, J., *J. Biochem. Japan*, **17**, 395 (1933); *Chem. Abs.*, **27**, 5103 (1933).

²² Viale, G., *Riv. sudamer. endocrinol. immunol. quimio-terap.*, **17**, 547 (1934); *Chem. Abs.*, **28**, 6794 (1934); Lund, H., and Lieck, H., *Skand. Arch. Physiol.*, **74**, 269 (1936); Martini, E., *Biochim. terap. sper.*, **20**, 505 (1933); *Chem. Abs.*, **28**, 3456 (1934).

²³ Martini, E., and Bonsignore, A., *Boll. soc. ital. biol. sper.*, **9**, 388 (1934); *Chem. Abs.*, **28**, 6460 (1934); Bonsignore, A., *Boll. soc. ital. biol. sper.*, **10**, 62 (1935); *Chem. Abs.*, **29**, 3385 (1935).

²⁴ Cornbleet, T., *Arch. Dermatol. Syphilol.*, **35**, 471 (1937); *Chem. Abs.*, **31**, 5412 (1937).

²⁵ Buruiană, L., *Biochem. J.*, **31**, 1452 (1937).

Vitamins of the B Group. During the early difficult period when the multiplicity of the water-soluble vitamins other than ascorbic acid was being investigated and when but two such products were definitely recognized, attempts were made, in anticipation of any knowledge of their structure or absorption spectra, to differentially destroy one but not the other by the aid of ultraviolet light. This treatment was intended to be applied to yeast used in experimental diets for the production of deficiencies, the growth factor other than B_1 being the more susceptible.²⁶ Kennedy and Palmer²⁷ doubted that such methods could be relied upon, since both factors could be destroyed, but with varying ease. Hogan and Hunter showed that autoclaving had the opposite effect, destroying the antineuritic factor more rapidly than the growth factor. Hogan and Richardson²⁸ claimed to have attained satisfactory results in the destruction of the antidermatitis factor by mercury-arc irradiation. Guerrant and Salmon²⁹ found the destruction of the growth-promoting factor to proceed more rapidly when the irradiation was applied to an alkaline solution. After the later recognition of the flavins as growth-promoting factors, Hogan and Richardson³⁰ reinvestigated the matter and concluded that in irradiation of the diets both the flavins and an unidentified factor essential for the prevention of dermatitis are destroyed. It has since been shown by others that the rat antidermatitis factor is pyridoxine [2-methyl-3-hydroxy-4,5-di-(hydroxymethyl)-pyridine]. In the determination of its structure, ultraviolet absorption spectra gave important information. Nicotinic acid, the antipellagra factor, has an absorption maximum at about 2600A.³¹

Contrary to these observations, Halliday and Evans³² state that none of the factors present in brewers' yeast extract was destroyed by ten hours of irradiation. Doubtless this result is to be ascribed to the presence of substances in the extracts which act as internal filters. It is now known that B_1 (thiamine), the flavins and nicotinic acid can be destroyed when solutions of the pure substances are irradiated by ultraviolet light (visible light in the case of the flavins). György³³ finds a pellagra-preventing factor to be destroyed by visible light, at the same time changing from yellow to brown.

Before the chemical purification of B_1 concentrates had advanced to a stage in which sulfur was recognized as a constituent of the compound, attempts were made to prepare the vitamin from various precursors. Heyroth and Loofbourow³⁴ called attention to the resemblance of the ultraviolet absorption spectra of highly purified concentrates to the spectra of purines and pyrimidines and noted that irradiation of the latter with ultraviolet light from which the shorter wave-lengths had been excluded seemed to increase the resemblance. They showed, however,³⁵ that irradiated nucleic acids and irradiated uracil lacked antineuritic and growth-promoting properties. Guha³⁶ claimed to have been successful in producing the antineuritic vitamin by the irradiation of adenine. Other workers confirmed the observations of Heyroth that the vitamin

²⁶ Hogan, A. G., and Hunter, J. E., *J. Biol. Chem.*, **78**, 433 (1928).

²⁷ Kennedy, C., and Palmer, L. S., *J. Biol. Chem.*, **83**, 493 (1929).

²⁸ Hogan, A. G., and Richardson, L. R., *Mo. Agr. Exp. Sta. Research Bull.*, **178**, 3 (1932).

²⁹ Guerrant, N. B., and Salmon, W. D., *J. Biol. Chem.*, **89**, 199 (1930).

³⁰ Hogan, A. G., and Richardson, L. R., *Nature*, **136**, 186 (1935); *Science*, **83**, 17 (1936); *Mo. Agr. Exp. Sta., Bull.* **340**, 26 (1934).

³¹ Compare the absorption of a growth-factor called B_2 by Karrer, P., and von Euler, H., *Arch. Kemi. Mineral Geol.*, **11B**, No. 16 (1933); *Chem. Abs.*, **27**, 5101 (1933).

³² Halliday, N., and Evans, H. M., *J. Biol. Chem.*, **118**, 255 (1937).

³³ György, P., *Biochem. J.*, **29**, 767 (1935).

³⁴ Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Science Research*, **3**, 237 (1931).

³⁵ Heyroth, F. F., and Loofbourow, J. R., *Nature*, **131**, 92 (1933); *Bull. Basic Science Research*, **4**, 119 (1932).

³⁶ Guha, B. C., *Nature*, **130**, 741 (1932). Bonner, J., and Greene, J., [*Botan. Gaz.*, **100**, 226 (1938); *Chem. Abs.*, **32**, 9185 (1938)] believe the thiamin content of pea plants increases in light.

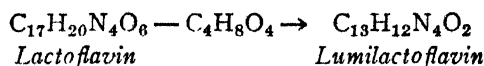
cannot be produced by the irradiation of a simple purine or pyrimidine³⁷ and Guha and Chakravorty³⁸ later admitted that irradiated adenine does not cure avian polyneuritis, although they still believed it to have growth-promoting properties. This Schultz and Laquer suggest may have been due to a contamination of the adenine used by one of the growth-promoting vitamins of the B group.

Heyroth and Loofbourow³⁹ later studied samples of crystalline thiamine (B₁) as well as concentrates of varying degrees of purity. It was shown that pure thiamine had absorption maxima at about 2650Å and 2350Å. Ultraviolet irradiation destroys the physiological activity and reduces the extinction coefficients.⁴⁰ An oxidation product, thiochrome, which has an intense fluorescence employed for assay purposes, is rapidly destroyed by ultraviolet light.⁴¹

Absorption studies and observations of the destructive effects of irradiation with visible light have played an important part in the development of our knowledge of the flavins as growth-promoting vitamins. The brilliant green fluorescence of these materials led to their discovery and guided their isolation. That the flavins in aqueous alkaline solution could be photochemically inactivated by visible light was shown in one of the first papers dealing with these substances.⁴²

During this process there was produced a colored substance soluble in chloroform, which came to be known as a lumiflavin or lumichrome.⁴³

It was shown by Kuhn and Wagner-Jauregg⁴⁴ that the photolysis consists in the splitting off of an oxygen-rich, nitrogen-free group of atoms:



Other flavins, such as uroflavin, maltoflavin and hepatoflavin were shown to undergo a similar photolysis,⁴⁵ which involves the loss of a sugar-like side-chain. In searching for analogies for this behavior, Kuhn and Bär⁴⁶ showed that when 2-tetraoxybutylquinoxaline is irradiated in alkaline solution, the tetraoxybutyl residue held on a carbon atom is replaced by an atom of hydrogen with the formation of the chloroform-soluble quinoxaline. In this case, however, the original compound was colorless so that it was necessary to employ ultraviolet light.

Similarly, Ohle⁴⁷ found the closely related 3-tetraoxybutyl-2-oxyquinoxaline loses not four but three carbon atoms as glycerin and yields 2-oxyquinoxaline-3-aldehyde. Irradiation of an alkaline solution of pentahydroxyamyl-benzimidazole

³⁷ Schultz, F., and Laquer, F., *Z. physiol. Chem.*, **219**, 158 (1933); Sure, B., *Biochem. J.*, **27**, 2043 (1933); Yamamoto, R., and Yamagishi, T., *J. Agr. Chem. Soc. Japan*, **9**, 749 (1933); *Chem. Abs.*, **27**, 5381 (1933). It was early shown that irradiation of a polyneuritic animal has no favorable effects. Krizenecky, J., *Arch. ges. Physiol. (Pflüger's)*, **204**, 407 (1924); **211**, 663 (1926); *Chem. Abs.*, **20**, 1437 (1926).

³⁸ Guha, B. C., and Chakravorty, P. N., *Nature*, **132**, 447 (1933), *J. Indian Chem. Soc.*, **11**, 195 (1934); *Chem. Abs.*, **28**, 5503 (1934).

³⁹ Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Sci. Research*, **4**, 35 (1932); *Nature*, **134**, 461 (1934); *Biochem. J.*, **30**, 651 (1936), see also Peters, R. A., and Philpot, J., *Proc. Roy. Soc.*, **B113**, 48 (1931); Holiday, E. R., *Biochem. J.*, **29**, 719 (1935); Wintersteiner, O., Williams, R. R., and Ruehle, A. E., *J. Am. Chem. Soc.*, **57**, 517 (1935).

⁴⁰ Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **56**, 2010 (1934); Kakefuda, H., *Fukuoka Acta Med.*, **27**, 99 (1934); *Chem. Abs.*, **29**, 6278 (1935).

⁴¹ Otto, H., and Rühmekorb, F., *Klin. Wochschr.*, **17**, 1246 (1938); *Chem. Abs.*, **32**, 9133 (1938).

⁴² Kuhn, R., György, P., and Wagner-Jauregg, T., *Ber.*, **66**, 317 (1933).

⁴³ Ellinger, P., and Koschara, W., *Ber.*, **66**, 808, 1411 (1933).

⁴⁴ Kuhn, R., and Wagner-Jauregg, T., *Ber.*, **66**, 1577 (1933); Kuhn, R., Rudy, H., and Wagner-Jauregg, T., *Ber.*, **66**, 1950 (1933).

⁴⁵ Stern, K. G., *Nature*, **133**, 178 (1934); Koschara, W., *Z. physiol. Chem.*, **229**, 103 (1934); Bierry, H., and Gouzon, B., *Compt. rend.*, **200**, 2116 (1935); *Chem. Abs.*, **29**, 6911 (1935).

⁴⁶ Kuhn, R., and Bar, F., *Ber.*, **67**, 898 (1934).

⁴⁷ Ohle, H., *Ber.*, **67**, 155 (1934).

gives a small amount of benzimidazole; the main photochemical product was not identified.⁴⁸

It was later shown by Kuhn and Rudy⁴⁹ that during the loss of the sugar-like side-chain in the photolysis of the flavin an alkyl group becomes attached to a nitrogen atom. After much further work, it has been shown that lumilactoflavin is 6,7,9-trimethylisoalloxazine.⁵⁰

In work on the synthesis of substances similar to lactoflavin, Karrer, Schlittler, Pfachler and Benz⁵¹ noted that their synthetic 9-(betahydroxyethyl) isoalloxazine when irradiated by sunlight in neutral solution gave 9-methylisoalloxazine. In alkaline solution, irradiation gave alloxazine and its 9-methyl derivative. Lumichrome was also obtained from ovoflavin⁵² and lactoflavin.⁵³ Karrer attributes the light-sensitivity of lactoflavin to the presence of a single β -hydroxyl group in the sugar-like side-chain.

When a synthetic branched-chain flavin, 9-(2',3'-dihydroxy-1'-isopropyl)-isoalloxazine, is illuminated in water or methanol solution, it slowly breaks down yielding some alloxazine, the decomposition appearing to start at the hydroxyl in the 2' position of the side-chain. In alkaline solution, however, easily soluble colorless compounds were formed by the action of light, and no alloxazine could be detected.⁵⁴ The decomposition by sunlight of a flavin containing a tertiary hydroxyl group, such as 9-(2'-hydroxy-2'-methyl-1'-propyl)isoalloxazine, however, shows⁵⁵ that it is not necessary that dehydrogenation occur at the 2' position of the hydroxy side-chain. The rate of decomposition is much slower with this compound than with flavins containing a primary or a secondary group. As with the other flavins, the photolysis proceeds more rapidly in aqueous methanol than in water.

Subsequently, Karrer, Köbner, Salomon and Zehender⁵⁶ drew more clearly the distinction between the decomposition of lactoflavin to lumichrome (that is, alloxazine) derivatives which occurs in neutral solutions and that of γ -hydroxypropyl isoalloxazine, which fails to react in neutral solutions but is rapidly decomposed to alloxazine in alkaline solutions. The former reaction is said to be a dehydration commencing by oxidation at the β -CHOHCO.⁵⁷

Flavins may exert a photo-sensitizing action upon ascorbic acid since its oxidation potential falls in light more rapidly in their presence than in their absence.⁵⁸

The brilliant fluorescence of the flavins has been employed in this essay,⁵⁹ and practical rapid methods for the application of the Fluoray lamp to the assay of flavins in milk have been given by Whitnah, Kunerth and Kramer⁶⁰ and by Supplee, Ansbacher, Flanigan and Hanford.⁶¹

⁴⁸ Kuhn, R. and Bar, F., *Ber.*, **67B**, 898 (1934); Kuhn and Weygand, F., *Ber.*, **67B**, 1939 (1934).

⁴⁹ Kuhn, R., and Rudy, H., *Ber.*, **67**, 1298 (1934).

⁵⁰ Kuhn, R., Reinemund, K., and Weygand, F., *Ber.*, **67**, 1460 (1934); Kuhn, R. and Rudy, H., [*Ber.*, **67B**, 1936 (1934)] state that lumichrome, similarly formed by irradiation in neutral or acid solutions is 6,7-dimethylalloxazine.

⁵¹ Karrer, P., Schlittler, E., Pfachler, K., and Benz, F., *Helv. Chim. Acta*, **17**, 1516 (1934).

⁵² Karrer, P., and Schöpp, K., *Helv. Chim. Acta*, **17**, 1557 (1934).

⁵³ Karrer, P., Salomon, H., Schöpp, K., Schlittler, E., and Fritzsche, H., *Helv. Chim. Acta*, **17**, 1010 (1934).

⁵⁴ Karrer, P., and Meerwein, H., *Helv. Chim. Acta*, **18**, 480 (1935).

⁵⁵ Karrer, P., and Meerwein, H., *Helv. Chim. Acta*, **18**, 1126 (1935).

⁵⁶ Karrer, P., Köbner, T., Salomon, H., and Zehender, F., *Helv. Chim. Acta*, **18**, 266 (1935).

⁵⁷ For further details concerning the structure of related compounds as affecting the photolysis, see, Karrer, P., and Musante, C., *Helv. Chim. Acta*, **18**, 1134 (1935); Karrer, P., Köbner, T., and Zehender, F., *Ibid.*, **19**, 261 (1936); Karrer, P., and Naef, R., *Ibid.*, **19**, 1029 (1936).

⁵⁸ Martini, E., *Boll. soc. ital. soc. biol. sper.*, **9**, 1235 (1934); *Chem. Abs.*, **29**, 2580 (1935); Süllmann, H., *Klin. Wochschr.*, **17**, 1157 (1938); *Chem. Abs.*, **32**, 8273 (1938).

⁵⁹ Josephy, B., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **4**, 46 (1934); *Chem. Abs.*, **29**, 3362 (1935); Cohen, F. H., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **4**, 46 (1934); *S. 18* (1935); *Chem. Abs.*, **29**, 4044, 4790, 5482 (1935); *Rec. trav. chim.*, **54**, 133 (1935); Bierry, H., and Gouzon, B., *Compt. rend. soc. biol.*, **119**, 101 (1935); *Chem. Abs.*, **29**, 5133 (1935); Karrer, P., and Fritzsche, H., *Helv. Chim. Acta*, **18**, 911 (1935); van Eekelen, M., and Emmerie, A., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **5**, 77 (1935); Weisberg, S. M., and Levin, I., *Ind. Eng. Chem. (Anal. Ed.)*, **9**, 523 (1937).

⁶⁰ Whitnah, C. H., Kunerth, B. L., and Kramer, M. M., *J. Am. Chem. Soc.*, **59**, 1153 (1937).

⁶¹ Supplee, G. C., Ansbacher, S., Flanigan, G. E., and Hanford, Z. M., *J. Dairy Sci.*, **19**, 215 (1936).

It must also be noted that the methods of irradiation which proved so helpful in the study of the constitution of the flavins had in fact been based upon similar previous observations of the behavior of a yellow oxidation enzyme obtained from yeast by Warburg and Christian,⁶² and which contains a flavin prosthetically bound to a protein. Observations by Theorell⁶³ show that so long as the active group (flavin phosphate) is combined with protein, it is unchanged by light, but when liberated in alkaline solution it behaves like lactoflavin. The destruction of the flavin or its ester proceeds more rapidly in the presence of oxygen than in its absence, but more rapidly in air than in pure oxygen. In an argon atmosphere, deuteroleucoflavin phosphate is first formed, and on continued irradiation in the absence of oxygen slowly splits to 6,7-dimethylalloxazine; on the admission of air, however, the unchanged leuco- compound is at once oxidized to deuteroflavin phosphate, which is rapidly split to dimethylalloxazine by light. Therefore, in the presence of air the deuterocompounds are not formed. In a strongly alkaline medium, the deuteroflavin is changed quantitatively to lumiflavin without the formation of dimethylalloxazine.

Vitamin A. Absorption spectrum studies have played a large part in the study of the constitution of vitamin A, as well as that of carotene which may replace it in the diet, being converted into the vitamin in the liver.⁶⁴

Morton and Heilbron⁶⁵ showed that vitamin A concentrates exhibit a prominent absorption band at 3285A, the intensity of which accords with the potency as determined by the depth of a blue color produced by antimony trichloride. In some fish oils, however, as in dogfish oil, the characteristic absorption band may be masked by absorption bands due to other substances. General confirmation of the absorption of the vitamin at 3280A was given by Drummond and Morton.⁶⁶ Evidence has been brought forward recently for the existence in the livers of certain fresh-water fishes of a second vitamin A, A₂, with an absorption maximum displaced to 3450-3500A.⁶⁷

The Hilger Vitameter has been introduced to facilitate the assay of vitamin A by measuring the 3280A band.⁶⁸ In the development of absorption assay methods

⁶² Warburg, O., and Christian, W., *Naturwiss.*, **20**, 980 (1932); *Biochem. Z.*, **258**, 496 (1933); British P. 430,571, June 17, 1935; *Chem. Abs.*, **29**, 7362 (1935).

⁶³ Theorell, H., *Biochem. Z.*, **279**, 186 (1935).

⁶⁴ Morton, R. A., "Applications of Absorption Spectra to the Study of Vitamins and Hormones," London, A. Hilger, Ltd.; Chevallier, A., *Bull. soc. chim. biol.*, **17**, 530 (1935); Rosenthal, J., and Weltner, M., *Biochem. J.*, **29**, 1036 (1935); De, N. K., *Indian J. Med. Research*, **22**, 509 (1935).

⁶⁵ Morton, R. A., and Heilbron, I. M., *Nature*, **122**, 10 (1928); *Biochem. J.*, **22**, 987 (1928).

⁶⁶ Drummond, J. C., and Morton, R. A., *Biochem. J.*, **23**, 785 (1929). Morton, R. A., Heilbron, I. M., and Spring, F. S., [*Biochem. J.*, **24**, 136 (1930)] answer certain objections raised by Rosenheim, O., and Webster, T. A., *Ibid.*, **23**, 633 (1929). See also Woodrow, J. W., and Cunningham, H. L., *Phys. Rev.*, **35**, 125 (1930); Woodrow, J. W., and Philipson, J. B., *Proc. Iowa Acad. Sci.*, **37**, 310 (1930); Coward, K. H., Dye, F. J., and Morton, R. A., *Biochem. J.*, **26**, 1593 (1932); Chevallier, A., and Chabre, P., *Biochem. J.*, **27**, 298 (1933); Joseph, B., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **3**, 133 (1933); *Chem. Abs.*, **28**, 2467 (1934); Crows, S. K., and Cox, S. J., *Analyst*, **59**, 85 (1934); *Chem. Abs.*, **28**, 2756 (1934).

⁶⁷ Gillam, A. E., Heilbron, I. M., Lederer, E., and Rosanova, V., *Nature*, **140**, 233 (1937); Edisbury, J. R., Morton, R. A., and Simpkins, G. W., *Ibid.*, **140**, 234 (1937); Lederer, E., and Rathmann, F. H., *Biochem. J.*, **32**, 1252 (1938). Compare (Chevallier, A., and Choron, Y., [*Compt. rend., soc. biol.*, **127**, 1443 (1938); *Chem. Abs.*, **32**, 6298 (1938)] who distinguish hemo- and hepato-forms of vitamin A.

⁶⁸ French P. 760,676, Feb. 28, 1934, to Adam Hilger Ltd; *Chem. Abs.*, **28**, 4180 (1934); British P. 416,423, Sept. 19, 1934; Twyman, F., and Follet, D. H., U. S. P. 2,065,953, Dec. 29, 1936, to Adam Hilger Ltd.; *Chem. Abs.*, **31**, 911 (1937); Irish, F. W., *J. Assoc. Off. Agr. Chem.*, **19**, 244 (1936); Wilkie, J. B., *Ibid.*, **20**, 208 (1937); Notevert, O., *Biochem. J.*, **29**, 1227 (1935); Baumann, C. A., and Steenbock, H., *J. Biol. Chem.*, **101**, 547 (1933); Baumann, C. A., Steenbock, H., Beeson, W. M., and Rupel, J. W., *Ibid.*, **105**, 167 (1934); Shrum, G. H., and How, T. G., *Can. J. Research*, **13A**, 93 (1935); McFarlane, W., and Rudolph, L., *Sci. Agr.*, **16**, 398 (1936); *Chem. Abs.*, **30**, 6405 (1936); Barthen, C. L., and Leonard, C. S., *J. Am. Pharm. Assoc.*, **26**, 515 (1937); Holmes, A. D., Black, A., Eckler, C. R., Emmett, A. D., Heyl, F. W., Neilsen, C., and Quinn, E. J., *Ibid.*, **26**, 525 (1937); *Chem. Abs.*, **31**, 6274 (1937); Nyveld, W. J., *Chem. Weekblad*, **34**, 379 (1937); *Chem. Abs.*, **31**, 7461 (1937); Leech, W. D., *Australian Chem. Inst. J. and Proc.*, **5**, 155 (1938); *Chem. Abs.*, **32**, 6281 (1938); McFarlane, R. L., and Reddie, J. W., U. S. P. 2,123,573, July 12, 1938; *Chem. Abs.*, **32**, 6510 (1938).

account must be taken of the absorption of carotene since that substance is physiologically equivalent to the vitamin. Its absorption spectrum is different,⁶⁹ lacking the band at 3280A. It has bands between 3300 and 3400A and between 2630 and 2950A.⁷⁰ The discovery of the conversion of carotene into vitamin A in the liver has been followed by spectrographic methods. Capper⁷¹ showed that the liver oil of rats deficient in vitamin A lacked its characteristic 3280A band and that this was present in the liver oil of rats which had been cured by the administration of carotene. Basu⁷² suggested that this change can occur only in animals receiving ultraviolet radiations. Bowden and Snow⁷³ believed that irradiation of β -carotene in cyclohexane produces a change in the absorption spectrum indicative of the production of vitamin A, but Dann⁷⁴ believes that this is precluded by the fact that the vitamin is more rapidly destroyed than is carotene by the 2650A line.

The extensive work on the assay of vitamin A by the spectrophotometric measurement of the intensities of colors produced on the addition of antimony trichloride lies beyond the scope of our present discussion.

The photochemical destruction of vitamin A has been very extensively studied. Earlier divergent findings were in large part due to the use of the antimony trichloride method, the results being somewhat masked by the effects of the several other chromogens which may accompany the vitamin in the oils and concentrates studied. It was first observed by Peacock⁷⁵ that the exposure of cod-liver oil to white light caused a loss of its fluorescence and of its ability to give the arsenic trichloride test then employed for the determination of the vitamin. The ability of the oil to promote growth in rats was lost. Confirmations were reported by Holmes and Pigott⁷⁶ and Titus, Hughes, Hinshaw and Fitch⁷⁷ stated that the irradiation of milk by a mercury arc caused a loss of some vitamin A. Zilva⁷⁸ reported that the irradiation of butter with ultraviolet light did not lead to the production of toxic substances as had been reported by Spinka.⁷⁹

Willmot and Wokes⁸⁰ irradiated cod-liver oil in an open dish only three inches from a mercury arc, the temperature rising to 70° in 90 minutes. One third of the vitamin A, determined by the colorimetric method, was destroyed in the first hour and the whole of it in two hours. They also noted that after a few minutes of irradiation, a slow destruction of the vitamin continued for a long period. Morton and Heilbron⁸¹ confirmed the results by noting the disappearance of the band

⁶⁹ Morton, R. A., and Heilbron, I. M., *Biochem. J.*, **24**, 870 (1930); Kawakami, K., *J. Agr. Chem. Soc. Japan*, **8**, 48 (1932); *Chem. Abs.*, **27**, 1661 (1933); Smith, J. H. C., *J. Am. Chem. Soc.*, **58**, 247 (1936).

⁷⁰ See also Woodrow, J. W., and Philipson, J. B., *Proc. Iowa Acad. Sci.*, **38**, 218 (1931); *Chem. Abs.*, **27**, 2184 (1933); Winterstein, A., *Z. physiol. Chem.*, **215**, 51 (1933); von Euler, H., and Klusmann, E., *Arkiv Kem., Mineral. Geol.*, **11B**, No. 17 (1933); Miller, E. S., *Plant Physiol.*, **9**, 179 (1934); *Bot. Gaz.*, **96**, 447 (1935); *Plant Physiol.*, **10**, 375 (1935); Karer, P., and Solmssen, U., *Helv. Chim. Acta*, **18**, 25 (1935); Castle, D. C., Gillam, A. E., Heilbron, I. M., and Thompson, H. W., *Biochem. J.*, **28**, 1702 (1934). Carotene may be bleached by ultraviolet rays in treating cream for butter-making, according to H. E. Kistner, U. S. P. 2,119,461, May 31, 1938; *Chem. Abs.*, **32**, 5526 (1938).

⁷¹ Capper, N. S., *Biochem. J.*, **24**, 980 (1930).

⁷² Basu, N. K., *Z. Vitaminforschung*, **3**, 254 (1934); *Chem. Abs.*, **29**, 5487 (1935).

⁷³ Bowden, F. P., and Snow, C. P., *Nature*, **129**, 720 (1932).

⁷⁴ Dann, W. J., *Biochem. J.*, **27**, 274 (1933); see also De, N. K., *Indian J. Med. Research*, **23**, 505 (1935).

⁷⁵ Peacock, P. R., *Lancet*, **II**, 328 (1926); *Science*, Oct. 15, 1926.

⁷⁶ Holmes, A. D., and Pigott, M. G., *Boston Med. Surg. J.*, **195**, 263 (1926).

⁷⁷ Titus, R. W., Hughes, J. S., Hinshaw, W. R., and Fitch, J. S., *Ind. Eng. Chem.*, **18**, 843 (1926).

⁷⁸ Zilva, S. S., *Biochem. J.*, **155**, 333 (1925).

⁷⁹ Spinka, J., *Biochem. Z.*, **153**, 197 (1924).

⁸⁰ Willmot, S. G., and Wokes, F., *Pharm. J.*, **118**, 217 (1927); *Chem. Abs.*, **21**, 3220 (1927); *Lancet*, **II**, 8 (1927); *Chem. Abs.*, **22**, 257 (1928).

⁸¹ Morton, R. A., and Heilbron, I. M., *Nature*, **122**, 10 (1928).

at 3280A. Their absorption studies indicated that the first decomposition products of the vitamin might possess an absorption band in the region 2750 to 2850A. A very rich shark-liver oil was employed. Steenbock and Wirick⁸² found the destruction of the vitamin in butter-fat to be proportional to the time of irradiation and inversely proportional to the thickness of the layer exposed. The process could be retarded by surrounding the fat with an inert gas.

Norris⁸³ used both colorimetric and biological assays and conducted the irradiation of cod-liver oil in a rotating closed quartz cylinder under carbon dioxide, at a temperature not over 15°C. Preliminary work indicated an induction period of about two hours, although in subsequent experiments⁸⁴ this could be confirmed only for the biological assays. A plot of the reciprocals of the chromogen which with antimony trichloride gives absorption between 600 and 617 m μ against the time of exposure gave a straight line. The vitamin content reached zero after about four hours.

By colorimetric determinations, Evers⁸⁵ found little or no change in the first two hours, after which there was a slow change. Hawk⁸⁶ reported an actual increase in the antimony trichloride blue color during irradiation in air. Although denied by Drummond,⁸⁷ this observation was confirmed by Norris and Church⁸⁸ and by Heilbron, Gillam and Morton.⁸⁹

Wave-lengths shorter than 3350 to 3400A are required for the destruction of the vitamin⁹⁰

Chevallier⁹¹ found carbon-arc irradiation of a hexane solution of an unsaponifiable vitamin A concentrate to produce a rapid destruction of the absorption band at 3280A. At the same time there was evidence from the absorption changes within the region 2900 to 3400A⁹² of the production of new products which in turn were destroyed at different rates. One product formed may be an intermediate between vitamin A and β -ionone.⁹³ From the results of the use of filtered light of 3650A Chevallier and Dubouloz⁹⁴ calculated the quantum yield as 1/28, and noted that the decomposition follows a somewhat different course in slightly acid and in slightly alkaline ethanol. It is claimed that the formation of several decomposition products may be recognized by analysis of the spectrographic results.⁹⁵

⁸² Steenbock, H., and Wirick, A. M., *J. Dairy Sci.*, **14**, 229 (1931); *Chem. Abs.*, **25**, 4030 (1931); Shrewsbury, C. L., and Kraybill, H. R., *Science*, **75**, 86 (1932).

⁸³ Norris, R. J., *Bull. Basic Sci. Research*, **3**, 89 (1931).

⁸⁴ Nabarro, D., and Hickman, J. O., found no change in thirty seconds, *Lancet*, **I**, 127 (1930).

⁸⁵ Evers, N., *Quart. J. Pharm.*, **2**, 556 (1929); *Brit. Chem. Abs.*, **A**, 1203 (1929).

⁸⁶ Hawk, P. B., *Science*, **69**, 200 (1929).

⁸⁷ Drummond, I. C., *J. Soc. Chem. Ind.*, **49**, 285T (1930).

⁸⁸ Norris, E. R., and Church, A. E., *J. Biol. Chem.*, **89**, 421 (1930).

⁸⁹ Heilbron, I. M., Gillam, A. E., and Morton, R. A., *Biochem. J.*, **25**, 1352 (1931). Even the 3280A band increases during the first few minutes of irradiation, according to Boyle, E., *Nature*, **133**, 798 (1934); *Biochem. J.*, **28**, 573 (1934). See also Smith, E. L., Stern, B. E., and Young, F. E., [*Nature*, **141**, 551 (1938)] who find that irradiation sometimes increases and sometimes decreases the absorption, which, however, returns to normal on standing in the dark. These changes may be due to *cis-trans* isomerization. Morton, R. A., *Nature*, **141**, 552 (1938).

⁹⁰ Norris, R. J., and Loofbourrow, J. R., *Bull. Basic Sci. Research*, **4**, 113 (1932).

⁹¹ Chevallier, A., *Compt. rend. soc. biol.*, **112**, 1681 (1933); *Chem. Abs.*, **27**, 3974 (1933).

⁹² Chevallier, A., and Choron, Y., *Compt. rend. soc. biol.*, **115**, 1297 (1934); *Chem. Abs.*, **28**, 4455 (1934).

⁹³ Chevallier, A., Choron, Y., and Guillot, J., *Compt. rend. soc. biol.*, **117**, 10 (1934); *Chem. Abs.*, **29**, 201 (1935).

⁹⁴ Chevallier, A., and Dubouloz, P., *Bull. soc. chim. biol.*, **18**, 190, 703 (1936); *Brit. Chem. Abs.*, **A**, 1159 (1936).

⁹⁵ Chevallier, A., Dubouloz, P. and Manuel, S., *Compt. rend. soc. biol.*, **121**, 1415 (1936); Dubouloz, P., *J. chim. phys.*, **33**, 532 (1936); Chevallier, A. and Dubouloz, P., *Bull. soc. chim. biol.*, **18**, 1115 (1936).

Chevallier uses the changes in absorption at 3250A during irradiation in a method for the spectrographic assay for vitamin A.⁹⁶

Dried spinach loses 70 per cent of its vitamin A during fifteen months of storage in diffused light. Ultraviolet light also decolorizes a petroleum ether extract of carrots and destroys its vitamin A action.⁹⁷ Alfalfa leaves bleached in sunlight also show a loss of vitamin A.⁹⁸ The same is true of ghee.⁹⁹

The decolorization of carotene is also accelerated by ultraviolet light¹⁰⁰ and it may be this which is changed in alfalfa.¹⁰¹ Some observations on the photo-oxidation of α -carotene in ultraviolet light, reported by Baur,¹⁰² indicate an induction period, after which the course of the oxygen uptake in chloroform solution is autocatalytic. There may be a reversible formation of a photo-oxide. The changes in absorption spectra of carotene and xanthophyll have been followed during their slow oxidation by McNicholas.¹⁰³

Kuhn and Winterstein¹⁰⁴ have isolated from saffron a dimethyl ester of a substance isomeric with crocetin. It is converted into crocetin by the action of blue or violet, but not of red, light. Radiations of wave-lengths less than 4150A are not essential to the reaction. The isomerization may be of the *cis-trans* type.

Vitamin E.¹⁰⁵ Ultraviolet irradiation destroys absorption bands at 2860 to 3200A at the same time that the activity of a concentrate is diminished, according to Bowden and Moore.¹⁰⁶ Bands at 2400 to 2850A are unaltered. The association of a band at 2940A with the biological activity is confirmed by Drummond, Singer and MacWalter,¹⁰⁷ who also find it to be diminished by irradiation. Olcott,¹⁰⁸ however, believes this band due not to the vitamin but to some closely related, difficultly removable substance.

Extracts of the antihemorrhagic vitamin retain their potency after 24 hours of exposure in a sealed tube to the light of a 500-watt lamp at three to four inches.¹⁰⁹ Later, Almquist^{109a} showed direct sunlight to destroy the vitamin.

The protective factor against nutritional encephalomalacia in chicks is also resistant to ultraviolet irradiation.¹¹⁰

PHOTOCHEMISTRY OF VISION.

It is only possible to note briefly that there has recently been a growing interest in the mechanism of vision. The photochemical changes involved are believed to

⁹⁶ Chevallier, A., *Z. Vitaminforsch.*, **7**, 10 (1938); *Chem. Abs.*, **32**, 5016 (1938).

⁹⁷ Quinn, E. J., Hartley, J. G., and Derow, M. A., *J. Biol. Chem.*, **89**, 657 (1930).

⁹⁸ Smith, M. C., and Briggs, I. A., *J. Agr. Research*, **46**, 229, 235 (1933), (*Chem. Abs.*, **27**, 235 (1933)); Douglass, E., Tobolska, J. W., and Vail, C. E., *Colorado Agr. Exp. Sta. Tech. Bull.*, **4**, 68pp. (1933); *Chem. Abs.*, **28**, 3449 (1934).

⁹⁹ Banerjee, B. N., and Dastut, N. N., *Agr. Live-Stock, India*, **6**, 433 (1936); *Chem. Abs.*, **31**, 471 (1937).

¹⁰⁰ Oleovich, H. S., and Mattill, H. A., *J. Biol. Chem.*, **91**, 105 (1931); *Chem. Abs.*, **25**, 3697 (1931).

¹⁰¹ Russell, W. C., Taylor, M. W., and Chichester, D. F., *New Jersey Agr. Exp. Sta. Bull.*, **560**, 1 (1934); *Chem. Abs.*, **28**, 6788 (1934).

¹⁰² Baur, E., *Helv. Chim. Acta*, **19**, 1210 (1936); **20**, 402 (1937).

¹⁰³ McNicholas, H. J., *Bur. Standards Research*, **7**, 171 (1931).

¹⁰⁴ Kuhn, R., and Winterstein, A., *Ber.*, **66B**, 209 (1933).

¹⁰⁵ For tentative absorption spectra, Bowden, F. P., and Moore, T., *Nature*, **121**, 512 (1933); von Euler, H., Hellström, H., and Klusmann, E., *Svensk Kem. Tid.*, **45**, 132 (1933); *Chem. Abs.*, **27**, 4284 (1933); Morton, R. A., and Edisbury, J. R., *Nature*, **131**, 618 (1933); Martin, A., Moore, T., Schmidt, M., and Bowden, F. P., *Ibid.*, **134**, 214 (1934).

¹⁰⁶ Bowden, F. P., and Moore, T., *Nature*, **132**, 201 (1933).

¹⁰⁷ Drummond, J. C., Singer, E., and MacWalter, R. J., *Biochem. J.*, **29**, 456 (1935).

¹⁰⁸ Olcott, H. S., *J. Biol. Chem.*, **110**, 695 (1935).

¹⁰⁹ Almquist, H. J., *J. Biol. Chem.*, **114**, 241 (1936).

^{109a} Almquist, H. J., *J. Biol. Chem.*, **117**, 517 (1937); MacCorquodale, D. W., Binkley, S. B., McKee, R. W., Thayer, S. A., and Doisy, E. A., *Proc. Soc. Exptl. Biol. Med.*, **40**, 482 (1939).

¹¹⁰ Goettsch, M., and Pappenheimer, A. M., *J. Biol. Chem.*, **114**, 673 (1936).

occur in substances in two different histological structures, the rods scattered throughout much of the retina but particularly toward the periphery, and the cones localized near the fovea.¹¹¹ The changes in the former, effected principally during vision in dim light, are not concerned with color sensation, as are the changes in cones which are brought about primarily by bright light.

The processes are regarded as deviations from photochemical stationary states set up during the period of accommodation to light of various intensities. Little is known as yet as to the photochemistry of materials in the cones.¹¹² The possibility that a flavin, known to occur in the retina, may be concerned with color vision and thus have to do in some manner with processes occurring in the cones has been mentioned by Theorell.¹¹³

Since the pioneering observations of Boll in 1877¹¹⁴ it has been known that the rods contain a substance known as the visual purple, which is bleached by light. Weigert and Nakashima¹¹⁵ investigated the photodichroism of the product as obtained from the retinas of frogs and spread in gelatin layers upon glass plates.

When applied to photographic plates, the visual purple usually diminishes rather than increases their sensitivity, but Kögel,¹¹⁶ who reviewed the photochemical behavior of this material, observed a transient sensitization in a special case.

The bleaching of visual purple solutions in monochromatic light has been found to have a quantum efficiency of unity or very slightly less.¹¹⁷

The process is not one of oxidation, according to Brunner and Kleinau.¹¹⁸ The oxidation-reduction potential curves of solutions of visual purple have been investigated by Pincussen, Suzuki and Seitz.¹¹⁹ Kodama¹²⁰ has measured the glycolysis and oxygen consumption of the rat retina in light and in darkness. During the first thirty minutes, both the oxygen uptake and the aerobic glycolysis were much greater in darkness, but during the second thirty minutes the oxygen uptake diminished rapidly and approached the rate in light. The oxygen consumption was not proportional to the intensity of light with either continuous or short exposures. Aerobic glycolysis was but little influenced by the intensity of light. The gas exchange and oxygen consumption decreased temporarily in all cases in light, the latter showing the greater decrease. In colored light, the oxygen consumption was greatest in red, less in green and least in blue light. Aerobic glycolysis varied less, but in the same order. In sugar-free Ringer solution in darkness, the oxygen consumption was high at first but rapidly decreased to zero. The aerobic glycolysis was very low and quickly

¹¹¹ Hecht, S., *Physiol. Rev.*, **17**, 239 (1937); *J. Applied Phys.*, **9**, 156 (1938); Hartline, H. K., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 245 (1935).

¹¹² von Studnitz, G., *Arch. ges. Physiol. (Pflüger's)*, **239**, 515 (1937). Wald, G. [*Nature*, **140**, 545 (1937)] calls the violet cone pigment iodopsin. Vitamin A is probably related to it. Haig, C., Hecht, S. and Patek, A. J., Jr., *Science*, **87**, 534 (1938); Hecht, S. and Mandelbaum, J., *Ibid.*, **88**, 219 (1938).

¹¹³ Theorell, H., *Biochem. Z.*, **279**, 186 (1935).

¹¹⁴ Boll, F., *Arch. anat. Physiol.*, **4** (1877).

¹¹⁵ Weigert, F., and Nakashima, M., *Naturwiss.*, **17**, 840 (1929).

¹¹⁶ Kögel, G., *Phot. Korr.*, **65**, 138, 248 (1929); *Chem. Abs.*, **24**, 2068 (1930). Recent studies on the absorption spectrum of visual purple are due to Chase, A. M., and Haig, C., *J. Gen. Physiol.*, **21**, 411 (1938) and to Saito, Z., *Tohoku J. Exptl. Med.*, **32**, 432 (1938); *Chem. Abs.*, **32**, 9125 (1938).

¹¹⁷ Dartnall, H. J. A., Goodeve, C. F., and Lythgoe, R. J., *Proc. Roy. Soc. A*, **156**, 158 (1936); **A164**, 216 (1938); Lythgoe, R. J., and Goodeve, C. F., *Trans. Ophthalmol. Soc.*, **57**, 88 (1937); Goodeve, C. F., *Sci. J. Roy. Coll. Sci.*, **8**, 9 (1938).

¹¹⁸ Brunner, O., and Kleinau, W., *Monatsh.*, **68**, 244, 261 (1936).

¹¹⁹ Pincussen, L., Suzuki, T., and Seitz, E. O., *Biochem. Z.*, **272**, 357 (1934).

¹²⁰ Kodama, S., *Tohoku J. Exptl. Med.*, **28**, 423 (1936); *Chem. Abs.*, **31**, 1081 (1937).

dropped to zero. In the presence of 0.1 per cent sugar in the Ringer solution in darkness, the oxygen consumption, high at first, rapidly decreased to one-fifth of its original value, but the aerobic glucolysis decreased but slightly. In the presence of 0.4 per cent of sugar, the oxygen uptake and aerobic glucolysis were comparatively low at the start and decreased but very little. In darkness, anaerobic glucolysis was equally high in solutions containing 0.1, 0.2 and 0.4 per cent of sugar. Jongbloed and Noyons,¹²¹ also found the carbon dioxide production by frog retinas 22.5 per cent and the oxygen uptake 26.5 per cent greater in darkness than in white light.

Stutzke¹²² observed that when the dark-adapted beef retina is exposed to light, ammonia is liberated, the ammonia content increasing from 200 to 500 per cent. This effect, which can be inhibited by glucose, lactate or pyruvate, is not observed in the light-adapted retina.

More recent studies of the behavior of the visual purple have revealed intimate relationships not only to such compounds as trimethylamine and creatinine, but also to carotenes, vitamin A, and the flavins.¹²³

Observations on night blindness, a vitamin A deficiency,¹²⁴ led to the discovery of vitamin A in the normal retina. Wald¹²⁵ showed that mammalian retinas contain about 22 γ , and frog retinas 400 γ per gram of dry retina. The underlying pigment layers contain also xanthophyll. The function of the vitamin A is to serve as a precursor for the formation of the visual purple which is lost in the photochemical bleaching process. There is also present in the retina a faintly yellow pigment, known as retinene, of carotenoid nature. It does not occur free but associated with some other non-diffusible substance, probably a protein. In the light-adapted retina, the retinene is replaced by some vitamin A.

During vision the visual purple is converted photochemically into visual yellow which contains protein and retinene. This change is believed to be thermally reversible with regeneration of visual purple. Mirsky¹²⁶ suggests that the prosthetic group, retinene, is firmly bound in visual purple, and that the process of its bleaching to visual yellow consists in a denaturation of the protein after which the retinene is bound loosely if at all. He concludes the energy of activation of the denaturation to be low, the visual purple being denatured by a quantum of visible light. The function of the retinene in the visual purple may be to sensitize the protein denaturation to light.

When the visual yellow has been produced, it may either regenerate its precursor or lose some of its retinene which is then thermally converted into vitamin A and apparently lost to the retina by diffusion processes or in an unknown manner. This loss of visual purple has to be made up if night-blindness is to be averted, by a resynthesis by way of the underlying pigmented layer which Wald has shown to contain larger amounts of vitamin A. At least this is the case in the frog's eye, the retina of which has no blood supply.¹²⁷

Details of the effects of temperature, pH and seasonal variations on the bleach-

¹²¹ Jongbloed, J., and Noyons, A., *Z. Biol.* **97**, 399 (1936); *Chem. Abs.*, **31**, 2691 (1937).

¹²² Stutzke, S., *Klin. Wochschr.*, **15**, 524 (1936); *Chem. Abs.*, **30**, 6805 (1936).

¹²³ Brunner, O., *Oestern Chem. Ztg.*, **40**, 203 (1937); Wald, G., and Zussman, H., *Naturc.*, **140**, 197 (1937).

¹²⁴ Blegvad, O., *Am. J. Ophthalmol.*, **7**, 89 (1924); Fridericia, L. S., and Holm, E., *Am. J. Physiol.*, **73**, 63 (1925).

¹²⁵ Wald, G., *J. Gen. Physiol.*, **18**, 905 (1935); **19**, 781 (1936); *Nature*, **134**, 65 (1934).

¹²⁶ Mirsky, A. E., *Proc. Natl. Acad. Sci.*, **22**, 147 (1936). Krause, A. C., and Sidwell, A. E., Jr., *Am. J. Physiol.*, **121**, 215 (1938); *Arch. Ophthalmol.*, **18**, 807 (1937); suggest that the bleaching splits visual purple into protein and a colored lipid called visual yellow, which may be further bleached until colorless.

¹²⁷ See also Wald, G., and Clark, A. B., *J. Gen. Physiol.*, **21**, 93 (1937).

ing of visual purple have been reported by Chase,¹²⁸ who finds a photochemical decomposition product of certain retinal extracts to be an acid-base indicator, yellow in acid and colorless in alkaline solutions. He also states that the photodecomposition of the bile salt extracts of the retinas of summer frogs follows a first-order reaction course, but that of the extracts of winter frogs does not unless the extracts are made alkaline. The kinetics of the regeneration of bleached visual purple have recently been studied by Hecht, Chase, Schlaer and Haig.¹²⁹

Some attention has been devoted to the nature and function of other pigments, such as the orange intermediate between visual purple and the products of its complete bleaching,¹³⁰ and also to a blue-sensitive substance, possibly a flavin, which Chase believes may, after its decomposition, be concerned in the regeneration of the visual purple.¹³¹

Porphyropsin, a purple pigment from the retina of fresh-water fish, also goes through a cycle in light, involving russet and yellow pigments.¹³² Stern and Salomon,¹³³ suggest that the first step in the bleaching of visual purple may be a photodissociation of ovoverdin, rather than a denaturation of the protein carrier.

¹²⁸ Chase, A. M., *J. Gen. Physiol.*, **19**, 577 (1936). See also Lythgoe, R. J., *J. Physiol.*, **89**, 331 (1937); Wald, G., *J. Gen. Physiol.*, **21**, 795 (1938).

¹²⁹ Hecht, S., Chase, A. M., Schlaer, S., and Haig, C., *Science*, **84**, 331 (1936). See also Hecht, S., Chase, A. M., and Schlaer, S., *Ibid.*, **85**, 567 (1937).

¹³⁰ Wald, G., *Nature*, **139**, 587 (1937).

¹³¹ Chase, A. M., *Science*, **85**, 484 (1937).

¹³² Wald, G., *Nature*, **139**, 1017 (1937).

¹³³ Stern, K. G., and Salomon, K., *Science*, **86**, 310 (1937).

Chapter 42

Photosensitized Biological Processes

The existence of a number of photosensitized reactions (discussed in Chapter 16) leads to the expectation that similar effects are to be encountered in biological processes. The first instance was reported by Raab from the laboratory of v. Tappeiner in 1899.¹ He observed that the dye acridine, in a dilution of 1:20,000, killed paramecia in six minutes in direct sunlight, in an hour in diffused light, and remained without effect for long periods in darkness. Many other dyes of widely different classes have similar effects, to which v. Tappeiner² applied the term "photodynamic actions."

Many recent workers have studied similar lethal effects on bacteria,³ fungi⁴ and various bacteriophages and viruses,⁵ as well as the destructive effects upon their toxins.⁶

The hemolysis of red cells may be similarly sensitized,⁷ notably by chlorophyll, which is effective even in dilutions of one in thirty million.⁸ Hematoporphyrin, a product of the decomposition of hemoglobin, as well as other porphyrins, exhibits such properties in a marked degree.⁹ When it is injected into mice no effects are produced until the animals are irradiated by sunlight or a carbon arc. Light causes itching, hyperemia of the ears, tail and snout, and, with sufficient doses of the sensitizer, the animals may die in light-stroke in a tetanic rigor. Desensitization occurs in darkness in about two weeks. The subject has been investigated to a considerable extent.¹⁰

¹ v. Tappeiner, H., *Z. Biol.*, **39**, 524 (1900)

² v. Tappeiner, H., *Deut. Arch. klin. Med.*, **80**, 427 (1904).

³ Brocq-Rousseau, D., *Compt. rend. soc. biol.*, **119**, 272 (1935); *Chem. Abs.*, **29**, 5474 (1935); Szűts, A., *Magyar Orvosi Arch.*, **33**, 267 (1932); *Chem. Abs.*, **27**, 323 (1933); Vorster, D., *J. Dental Research*, **9**, 641 (1929); *Chem. Abs.*, **24**, 133 (1930); Philibert, A. and Risler, J., *Compt. rend.*, **183**, 1137 (1926); **186**, 1152 (1928); Ram, A., *Proc. Acad. Sci. United Provinces, Agra, (Oudh, India)*, **4**, 83 (1934); Boyet, D., *Helv. Chim. Acta*, **17**, 1460 (1934); Tung, T., and Zia, S. H., *Proc. Soc. Exptl. Biol. Med.*, **36**, 326 (1937); Beck, L. V., and Nichols, A. C., *J. Cellular Comp. Physiol.*, **10**, 123 (1937); Tung, T., *Proc. Soc. Exptl. Biol. Med.*, **38**, 29 (1938); Chin, T. L., *Ibid.*, **38**, 697 (1938).

⁴ Gomez-Vega, P., *Arch. Dermatol. Syphilol.*, **32**, 49 (1935); *Chem. Abs.*, **30**, 572 (1936).

⁵ Clifton, C. E., *Proc. Soc. Exptl. Biol. Med.*, **28**, 745 (1931); Linden, H., and Schwarz, F. K. T., *Arch. Hyg.*, **106**, 133 (1931); Prescher, W., *Planta (Abt. E., Z. wiss. Biol.)*, **17**, 461 (1932); *Chem. Abs.*, **27**, 3968 (1933); Perdrau, J. R., and Todd, C., *Proc. Roy. Soc.*, **112B**, 188, 277 (1933); Galloway, T. A., *Brit. J. Exp. Path.*, **15**, 97 (1934); Storey, H. H., *Ann. Applied Biol.*, **21**, 588 (1934); *Chem. Abs.*, **29**, 2203 (1935); Sheboldaeva, A. D., and Shugladze, A. K., *Z. Microbiol. Epidemiol. Immunitätsforsch. (U.S.S.R.)*, **18**, 466 (1937); *Chem. Abs.*, **32**, 7504 (1938).

⁶ Lippert, K. M., *J. Immunol.*, **28**, 193 (1935); *Chem. Abs.*, **29**, 8048 (1935).

⁷ Gachs, H., and Sacharoff, G., *Munch. Med. Wochschr.*, **52**, 297 (1905); Saeki, K., *Japan J. Gastroenterol.*, **4**, 153, 166, 231, 244 (1932); *Chem. Abs.*, **27**, 1018 (1933); Angelica, V., *Boll. soc. ital. biol. sper.*, **8**, 1536 (1933); *Chem. Abs.*, **28**, 2767 (1934); Blum, H. F., Pace, N., and Garrett, R. L., *J. Cellular Comp. Physiol.*, **9**, 217 (1937).

⁸ Hausmann, W., *Jahr. Wiss. Botanik*, **46**, 599 (1909).

⁹ Kammerer, H., and Weisbecker, H., *Arch. Exptl. Path. Pharmacol.*, **111**, 263 (1926); Squires, B. T., *Biochem. J.*, **21**, 437 (1927).

¹⁰ Hausmann, W., and Löhner, L., *Biochem. Z.*, **173**, 7 (1926); Fabre, R., and Simonnet, H., *J. pharm. chim.*, **4**, 294 (1926); Supniewski, J. V., *J. Physiol.*, **64**, 30 (1927); *Chem. Abs.*, **22**, 455 (1928); Rock, E. N., and Howell, W. H., *Am. J. Physiol.*, **84**, 363 (1928); Smetana, H., *J. Exptl. Med.*, **47**, 593 (1928); Cuzin, J., *Bull. soc. chim. Biol.*, **12**, 1401 (1930); *Chem. Abs.*, **25**, 3368 (1931); Quin, J. I., *Rept. Director Vet. Services Onderstepoort*, **17**, Pt. 2, 645 (1931); *Chem. Abs.*, **27**, 5421 (1933); Szörenyi, E. T., *Biochem. Z.*, **252**, 113 (1932); *Boll. soc. ital. biol. sper.*, **7**, 835, 866 (1932); Robuschi, L., *Biochem. therap. sper.*, **23**, 54 (1936); *Chem. Abs.*, **30**, 5245 (1936); Hausmann,

Meyer-Betz¹¹ took 0.2 gram of hematoporphyrin intravenously. Irradiation by a carbon arc led to the production of a lesion which had some resemblance to those of hydroa. The immediate reaction was merely reddening and edema, but on the following day the area was infiltrated, reddened and painful, and rendered almost black by multiple hemorrhages. After a week, there was superficial necrosis, followed by the formation of a thick black scab. The sun produced on exposed areas a very severe dermatitis which began immediately after the exposure and progressed for several days. It was marked by extreme pain, swelling and induration, and was followed by a heavy pigmentation. Two cases of chronic porphyrinuria have recently been reported in which the face and hands were highly pigmented, although not hypersensitive to ultraviolet light.¹²

A disease in which there is marked sensitivity to light is the rare and usually fatal xeroderma pigmentosum or Kaposi's disease.

In human pathology, true light urticarias are rare.¹³ It has been suggested that hydroa vacciniforme represents a slight sensitization due to hematoporphyrin or other porphyrins produced by solar ultraviolet light from some precursor which was assumed to be present in the skin. The basis for this theory of the origin of the disease is the frequent association of a porphyrinuria. It may, however, be noted that porphyrinuria may occur from certain causes without causing light sensitivity.¹⁴

Certain diseases of animals have been attributed to photosensitization. After eating buckwheat, and especially the green parts of the plant, oxen, swine and sheep, on exposure to light, become greatly excited and dance about wildly because of the sensory stimulation of rapidly developing skin lesions. This disease, known to Hertwig as early as 1833, has been studied by Sheard, Caylor and Schlottbauer,¹⁵ who suggest that the sensitizer may be phylloporphyrin or possibly cholehematin.

The weed, St. John's wort, *Hypericum*, brings about similar symptoms in range animals, and it has been stated that Arabs used to stain their white horses with tobacco or henna to protect them from light in regions where this weed abounds. Ionnides¹⁶ isolated a pigment from the plant which photosensitized white rats, but its constitution is unknown.

A disease of sheep and Angora goats, Geelgikop, characterized by the sudden onset of a swelling of exposed parts of the head and ears,¹⁷ is caused by eating *Tribulus terrestris*.

W., and Kuen, F. M., *Biochem. Z.*, **265**, 105 (1933); Guerrini, G., *Boll. soc. ital. biol. sper.*, **6**, 401 (1931); *Chem. Abs.*, **26**, 772 (1932). Other substances may act, as trypanflavine, John, H., [*Biochem. Z.*, **155**, 159 (1925)], bacterial extracts, Risler, J., and Philibert, A., [*Compt. rend. soc. biol.*, **96**, 747 (1927)]; *Chem. Abs.*, **21**, 1844 (1927)], and bile, Condorelli, F., *Arch. fisiol.*, **28**, (1930); *Chem. Abs.*, **25**, 3711 (1931).

¹¹ Meyer-Betz, F., *Deut. Arch. Klin. Med.*, **122**, 476 (1913).

¹² Roth, E., *Deut. Arch. Klin. Med.*, **178**, 185 (1935). For congenital porphyrinuria in cattle, Rimington, C., *Onderstepoort J. Vet. Sci. Animal Ind.*, **7**, 567 (1936); *Nature*, **140**, 105 (1937); *Chem. Abs.*, **31**, 7108 (1937); Fröhlich, W., *Wien. Klin. Wochschr.*, **51**, 791 (1938); *Chem. Abs.*, **32**, 8510 (1938).

¹³ The relation of sensitization to light to dermatology has been reviewed by Eldinow, A., *Proc. Roy. Soc. Med.*, **28**, 633 (1935); Mathews, F. P., *Arch. Pathol.*, **23**, 399 (1937); *Chem. Abs.*, **31**, 5430 (1937). See also Ambrogio, A., *Arch. ital. dermatol. sifilol. venercol.*, **13**, 546 (1937); *Chem. Abs.*, **32**, 2216 (1938); Urbach, F., *Klin. Wochschr.*, **17**, 304 (1938); *Chem. Abs.*, **32**, 7116 (1938).

¹⁴ Hausmann, W., and Kuen, F. M., *Biochem. therap. sper.*, **21**, 441 (1934), *Chem. Abs.*, **29**, 1875 (1935).

¹⁵ Sheard, C., Caylor, H. P., and Schlottbauer, C. P., *J. Exptl. Med.*, **47**, 1013 (1928).

¹⁶ Ionnides, Z. M., *Arch. Inst. Pasteur Hollen.*, **2**, 161 (1928); *Chem. Abs.*, **25**, 1869 (1931), *Compt. rend. soc. biol.*, **105**, 349 (1930); *Chem. Abs.*, **25**, 1869 (1931).

¹⁷ Quin, J. L., and Rimington, C., *South African J. Sci.*, **30**, 461 (1933), *Chem. Abs.*, **28**, 2056 (1934); Quin, J., *Onderstepoort J. Vet. Sci.*, **1**, 459, 469, 497, 501, 505 (1933); **3**, 137 (1934); **4**, 463; *Chem. Abs.*, **28**, 2790 (1934); **29**, 7351 (1935); Rimington, C., Quin, J. L., and Roets, G. C. S., *Onderstepoort J. Vet. Sci. Animal Ind.*, **9**, 225 (1937); *Chem. Abs.*, **32**, 4660 (1938).

A wide variety of other physiological and pathological effects due to the action of light and sensitizers has been enumerated by Blum.¹⁸ Among others mentioned are the inhibition of clotting of the blood by fibrinogen in the presence of light and methylene blue, stimulation of nerves, contraction of isolated skeletal muscles bathed by the photosensitizer solution, and production of arrhythmias in the isolated turtle or mammalian heart perfused with photosensitizing solutions and exposed to light.

The hydrolysis of serum albumin may be effected by hematoporphyrin and oxygen in light.¹⁹ The porphyrin unites with the protein, becomes excited by the absorption of light, combines with oxygen and passes a part of its energy over to the protein molecule.

A number of generalizations have been made by Blum regarding these processes.²⁰ Although most sensitizers are fluorescent, the fluorescent rays they emit are not responsible for the effects produced and there is no quantitative relation between the fluorescence of a sensitizer and its biological effectiveness. The substances absorb chiefly in the visible range, and only the absorbed energy is effective biologically. (The possibility of sensitization to ultraviolet rays cannot be excluded.) Most of the effects produced by these substances in light can also be produced by them, although much more slowly, in darkness. The presence of oxygen appears to be essential for the processes occurring in light.²¹ Most effects in this category can be inhibited by blood serum and particularly by its albumin. Because of this action, the injection of dyes which hemolyze red blood cells *in vitro* is not followed by hemolysis in animals subsequently exposed to light.

Sensitization to various ultraviolet radiations may be effected by certain substances, such as acridine or tryptaflavine, which make the region in the vicinity of 3650A active.²² Ethyl chlorophyllide sensitizes especially to 3130 or 3650A, as well as to visible rays. Carotene sensitizes to the range of 2800 to 4350A, but in the shorter ultraviolet or visible rays is less effective than chlorophyll.²³

Attempts to utilize photodynamic substances in therapy have not proved encouraging. Kreidl and Nozicka²⁴ suggest that the therapeutic action of light may be promoted by injecting anthracene, anthraquinone or their derivatives. Eosin was at one time believed to cause a rapid loosening of necrotic tissues in luetic or tuberculous ulcers on exposure to sunlight. In connection with such attempts, it may be noted that urticarial reactions are readily produced. The intradermal injection of two drops of a 1:1000 solution of eosin renders the skin so sensitive that a few minutes of exposure to light produces an urticarial wheal.

An understanding of the mechanism of photosensitized biological processes is of importance because of the light it may cast upon the nature of the function of chlorophyll in the photosynthesis of carbohydrates. Noack²⁵ early divided photosensitizers into two classes: certain heavy metal salts and fluorescent organic dyes. Both serve as carriers of oxygen, the former by a change in valence of the metal

¹⁸ Blum, H. F., *Physiol. Rev.*, **12**, 23 (1932); Sellards, S. W., *J. Med. Research*, **38**, 293 (1918); Dognon, A., *Compt. rend. soc. biol.*, **98**, 283 (1928).

¹⁹ Boyd, M. J., *J. Biol. Chem.*, **103**, 249 (1933).

²⁰ See also Blum, H. F., *Biol. Bull.*, **59**, 81 (1930); *Chem. Abs.*, **26**, 4645 (1932).

²¹ Blum, H. F., and McBride, G. C., *Biol. Bull.*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932); Blum, H. F., *J. Cellular Comp. Physiol.*, **9**, 229 (1937); Speakman, C. R., and Blum, H. F., *Univ. Calif. Pub. Physiol.*, **8**, 147 (1937).

²² Kuen, F. M., and Rosenfeld, P., *Biochem. Z.*, **254**, 181 (1932).

²³ Kuen, F. M., and Püringer, K., *Biochem. Z.*, **286**, 196 (1936).

²⁴ Kreidl, I., and Nozicka, F., Austrian Patent, 142,163, June 25, 1935; *Chem. Abs.*, **29**, 6365 (1935). The claims that hematoporphyrin can enable visible light to cure rickets are doubtless in error in view of the work of Windaus on sensitized reactions of ergosterol. (Chapter 39.) Rezzani, F. D., *Biochem. therap. spec.*, **24**, 274 (1937); *Chem. Abs.*, **32**, 650 (1938). Tests by Marique, P. [*Bull. soc. chim. biol.*, **20**, 325 (1938); *Chem. Abs.*, **32**, 5039 (1938)] gave negative results.

²⁵ Noack, K., *Z. Botan.*, **12**, 273 (1920); *Chem. Abs.*, **15**, 2453 (1921).

and the latter by a formation of peroxides. The action of the latter substances can be stopped by such reducing agents as sodium sulfite. Gaffron²⁶ found that solutions of hematoporphyrin, chlorophyll or dyes in serums at pH 11.4 absorb oxygen on exposure to light with the oxidation of the protein to which the dyes become attached. Carbon dioxide and ammonia are liberated. The greater part of the former is ascribed to the action of acids liberated during oxidation upon the serum. Tyrosine, phenol and uric acid in alkaline solution can also be oxidized in this manner by dyes, such as eosin, erythrosin or Rose bengal. Aliphatic substrates are not so oxidized, according to Carter.²⁷ The introduction of an hydroxy or an amino-group renders benzene derivatives susceptible to this type of reaction. Side-chains in which the groups NH_2 and $\text{CH}=\text{CH}$ occur were oxidized, as were ring compounds, such as α -naphthol, tryptophane, tyrosine, thiophene and purine derivatives. Carter did not believe that hydrogen peroxide is formed in the process, which was neither accelerated by iron salts nor retarded by potassium cyanide.²⁸ Some have found such processes to be increased by cyanide.²⁹ Wohlgemuth and Szörényi believe that true tissue respiration is lowered from 2 to 18 per cent by visible or ultraviolet light. Sensitizers in darkness also reduce it. Illumination of tissue sections in the presence of hematoporphyrin or Rose bengal increases oxidation and this action is stimulated by cyanides. The true respiration, which they regard as distinct from this photooxidation, is believed to be reduced from 17 to 43 per cent. Sensitizers also decrease the usual stimulating effect of light on anaerobic glycolysis. In red cells, sensitizers produce methemoglobin especially when illuminated.³⁰ Hematoporphyrin increases the absorption of oxygen by red blood cells, especially in light, but there is no corresponding production of carbon dioxide. Photographic desensitizers as Pinakryptol green retard this.³¹ Attempts to isolate peroxides of fluorescent dyes which promote the transportation of oxygen in analogy with the assumed chlorophyll peroxide of Willstätter were unsuccessful, according to Gaffron.³² Acceptor peroxides were, however, produced during the photooxidation of aliphatic amines in the presence of chlorophyll. When a solution of chlorophyll in amylamine was exposed to light and then placed in darkness, the quantity of peroxidic oxygen was approximately equal to the amount of molecular oxygen absorbed. This oxygen was quantitatively evolved when a catalyst, such as manganese dioxide was added to the darkened solution. The photochemical action depended greatly upon the solvent chosen, increasing more than a hundred times when acetone or pyridine replaced water. The absorption of oxygen ultimately reached two molecules for each molecule of primary or secondary amine. Gaffron³³ dissolved ethyl chlorophyllid and allylthiourea in acetone and exposed the solution to monochromatic light in the presence of oxygen. The relation between the energy absorbed and the oxygen consumed was in agreement with the Einstein law, provided that the concentration of the acceptor was at least 7.5×10^{-1} moles per liter, or when the acceptor concentration was over 100 times that of the dye. Similar results were reported with hematoporphyrin as the dye.

²⁶ Gaffron, H., *Naturwiss.*, **13**, 859 (1925); *Biochem. Z.*, **179**, 157 (1926).

²⁷ Carter, C. W., *Biochem. J.*, **22**, 575 (1928).

²⁸ See also Blum, H. F., and McBride, G. C., *Biol. Bull.*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932).

²⁹ Bier, O. G., and Roche e Silva, M., *Compt. rend. soc. biol.*, **118**, 911, 914 (1935); *Chem. Abs.*, **29**, 3727 (1935); Wohlgemuth, J., and Szörényi, E., *Biochem. Z.*, **264**, 371, 389, 406 (1933).

³⁰ See also Choctetta, A., *Boll. soc. ital. biol. sper.*, **7**, 1545 (1932); *Chem. Abs.*, **27**, 2731 (1933).

³¹ Szörényi, E., *Biochem. Z.*, **252**, 113 (1932). See also Smetana, H., [*J. Biol. Chem.*, **124**, 667, 741, 745 (1938)] who finds the proteins of blood and the uric acid of urine the acceptors.

³² Gaffron, H., *Ber.*, **60B**, 2229 (1927).

³³ Gaffron, H., *Ber.*, **60B**, 755 (1927).

Blum and Spealman³⁴ believed the peroxide formed when fluorescent dyes alone are irradiated in aqueous solutions to be hydrogen peroxide formed from water and oxygen. They suggest that the bleaching of excited dye molecules may be due to their oxidation by the hydrogen peroxide.

There has been much discussion as to whether, in the dye-sensitized oxidations of various substances, it is the oxygen itself or the oxygen acceptor which receives the energy of the light-excited dye. Gaffron³⁵ does not believe the former can account for the facts. Even in cases in which it is the sensitizer itself which is oxidized, Gaffron believes that there are other molecules of the sensitizer which receive enough energy from the light-excited molecules to convert them into a long-lived form capable of being oxidized. Data on the quantum yields in the oxidation of rubrene were advanced in support of this view, but have recently been the subject of some discussion. (See Chapter 26.)

On the other hand, Kautsky and Hirsch,³⁶ in work on the oxidation of isoamylamine in the presence of chlorophyll, assumed that oxygen was activated by the transfer of energy from a metastable intermediary state of the pigment. The energy required for the activation of oxygen was calculated to be 37 kcal. (7620A). Energy of longer wave-lengths should not be able, therefore, to cause the reaction. To test this, Gaffron³⁷ filtered out practically all light of wave-length shorter than 7600A by the use of 6 mm. of B G 3, Schott glass. Bacterial pheophytin was used, since chlorophyll does not absorb in this range; thiosinamine was the acceptor. Since photooxidation still occurred, it seems that activation of oxygen is not the mechanism, and it must be the acceptor molecules which receive the energy of the excited dye. When organic substrates are oxidized in the presence of chlorophyll, one molecule of oxygen is used for each quantum of light absorbed regardless of the wave-length, except at wave-lengths where the quantum is too small and the reaction does not proceed. Further evidence that it is the oxygen-acceptor which acquires the energy has been given by Franck and Levi.³⁸ They suggest that the chlorophyll on absorption may form hydrogen and free radicals instead of forming a metastable excited molecule. These may subsequently reunite, with the production of a chemiluminescent glow. In the presence of oxygen, the hydrogen is oxidized. The acceptor takes over the energy absorbed by the chlorophyll. This offered a possible explanation of the fact that the fluorescence, which represents but a small part of the energy, is slightly extinguished by oxygen. The problem is still in a somewhat speculative state. Because of its relation to other photosensitized processes by which carbon dioxide and water are synthesized to carbohydrates in the green plant, the mechanism of these reactions is being actively investigated.

By continuously irradiating a dilute solution of sodium fluorescein, Menke³⁹ made a photofluorescein. It was separated by filtering after precipitation with a small amount of hydrochloric acid. After washing with water, the precipitated dye was dissolved in alkali and the sodium salt crystallized by careful evaporation. This material was then dissolved in Locke's solution so that each cc. contained a mg. of photofluorescein. It then hemolyzed rat blood in darkness to the same extent

³⁴ Blum, H. F., and Spealman, C. R., *J. Phys. Chem.*, **37**, 1123 (1933).

³⁵ Gaffron, H., *Biochem. Z.*, **264**, 251 (1933).

³⁶ Kautsky, H., and Hirsch, A., *Ber.* **64**, 2677 (1931); Kautsky, H., de Buijn, H., Neuwirth, R., and Baumeister, W., *Ber.* **66**, 1598 (1933); Kautsky, H., and Hirsch, A., *Biochem. Z.*, **278**, 374 (1935); Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, **68**, 152 (1935).

³⁷ Gaffron, H., *Ber.*, **68B**, 1409 (1935); *Chem. Abs.*, **29**, 8056 (1935).

³⁸ Franck, J., and Levi, H., *Naturwiss.*, **23**, 229 (1935).

³⁹ Menke, J. F., *Biol. Bull.*, **68**, 360 (1935); *Chem. Abs.*, **29**, 5871 (1935).

that fluorescein does in light, although the non-irradiated fluorescein had no apparent action in darkness. Approximately two hours in darkness were required for a 1:2000 dilution of the photofluorescein to hemolyze one cc. of 1 per cent red blood cells. Blum⁴⁰ believes that eosin dyes in dilute solutions show hemolysis of red blood cells in darkness only in the presence of hydrogen peroxide.

This résumé is necessarily too brief to give an adequate impression of the great number of investigations in this field which are of importance to the zoölogist or botanist rather than to the photochemist.⁴¹

That eosin and hematoporphyrin, when applied to the skin of mice and exposed for three months to sunlight, may produce skin tumors, has been noted by Büngeler.⁴² Certain carcinogenic agents, such as benzopyrene, shale oil and coal tar, exhibit a photodynamic action on paramecia.⁴³

⁴⁰ Blum, H. F., *Cold Spring Harbor Symposia Quant. Biol.*, 3, 318 (1935).

⁴¹ See, for further details: Kosman, A. J., and Lillie, R. S., *J. Cellular Comp. Physiol.*, 6, 505 (1935); *Chem. Abs.*, 29, 8098 (1935); Hinrichs, M., *Biol. Bull.*, 50, 1 (1926); Guerrini, G., *Boll. soc. ital. biol. sper.*, 8, 1357 (1933); *Chem. Abs.*, 28, 1726 (1934); Macht, D. I., *Proc. Soc. Exptl. Biol. Med.*, 23, 638, 639 (1926); Sunzeri, G., *Arch. fisiol.*, 33, 555 (1934); *Chem. Abs.*, 29, 1883 (1935); Welsh, J. H., *Biol. Bull.*, 66, 346 (1934); *Chem. Abs.*, 28, 346 (1934); Efimov, A., and Efimov, W. W., *Biochem. Z.*, 155, 376 (1925); Schanz, F., *Ber. botan. Ges.*, 41, 165 (1923); *Chem. Abs.*, 17, 3040 (1923); Blum, H. F., and Scott, K. G., *Plant Physiol.*, 8, 525 (1933); Jirovec, O., and Ziegler, Z., *Z. ges. Exptl. Med.*, 90, 651 (1933); *Chem. Abs.*, 29, 4031 (1935); Zikes, H., *Centr. Bakt. Parasitcnk.*, 11, 65, 128 (1925); *Chem. Abs.*, 20, 1423 (1926); Teplov, I., and Dobrokhotova, E., *Arch. sci. biol. U.S.S.R.*, 32, 72 (1932); *Chem. Abs.*, 27, 3492 (1933); Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, 22, 21 (1923); Roskin, G., and Romanova, K., *Z. Immunität.*, 72, 445 (1931); *Chem. Abs.*, 26, 2790 (1932); Azzi, A., *Arch. Sci. Med.*, 45, 212 (1922); *Chem. Abs.*, 17, 3541 (1923); Monasterio, G., *Arch. Pharmacol. Sper.*, 51, 111 (1930); *Chem. Abs.*, 25, 2486 (1931); Spealman, C. R., and Blum, H. F., *J. Cellular Comp. Physiol.*, 3, 397 (1933); *Chem. Abs.*, 28, 3089 (1934); Hinrichs, M. A., and Kosman, A. J., *J. Cellular Comp. Physiol.*, 6, 487 (1935); Lippay, F., *Klin. Wochschr.*, 6, 651 (1927); *Chem. Abs.*, 21, 2706 (1927); Nitta, B., *Folia Pharmacol. Japon.*, 17, 72 (1928); *Chem. Abs.*, 32, 3434 (1938); Kosman, A. J., *J. Cellular Comp. Physiol.*, 11, 279 (1938); *Chem. Abs.*, 32, 6677 (1938); Zia, S. H., Chow, B. F., and Tung, T., *Proc. Soc. Exptl. Biol. Med.*, 38, 688 (1938).

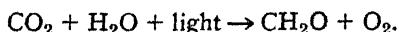
⁴² Büngeler, W., *Z. Krebsforsch.*, 46, 130 (1937); *Chem. Abs.*, 31, 8670 (1937)

⁴³ Mottram, J. C., and Doniach, I., *Nature*, 140, 933 (1937); *Lancet*, I, 1156 (1938).

Chapter 43

Photosynthesis of Carbohydrates¹

With the help of sunlight, the green plant builds up from carbon dioxide, water and salts the sugars and starches which serve as the foodstuffs of man. At the same time, oxygen is liberated. The photosynthetic process may be represented by the equation:



The hypothetical formaldehyde is assumed to be subsequently converted into sugars and starches. The energy required for this endothermic reaction must be supplied as light. This is absorbed by chlorophyll, the green pigment of the leaves, which in some as yet unknown manner acts as a photosensitizer for the reaction. The energy required for the synthesis of formaldehyde is at least 134 kcal., and possibly more.² Since the effective wave-lengths in the visible range may be as long as about 7000A, corresponding to only about 40 kcal., it is apparent that the absorption of one quantum per molecule would not provide sufficient energy to supply that needed for the reaction. It is essential, therefore, that at least three and more likely four quanta be absorbed for each molecule of carbon dioxide assimilated or of oxygen liberated. The nature of the coupled series of reactions underlying the photosynthetic process is not as yet understood, although ever-increasing attention has been devoted to the problem.

The investigations in this field may be divided into those concerned with the photochemical mechanism involved, as it might possibly be conceived of as occurring *in vitro* (in the presence of the extracted sensitizing pigment) and into those which actually occur in the plant. The latter studies belong in the realm of the plant physiologist and involve many complicated features, such as the influences of the stomatal openings within the leaf by which the gases gain entrance and egress, the nature and orientation of the chloroplasts (the histological regions within which the chlorophyll occurs), the amounts of energy reflected, absorbed and transmitted by the leaf, etc. For a discussion of these factors special works must be consulted.³ It is possible here to mention merely some calculations of the efficiency of the process as it occurs in an acre of corn, which have been made by Transeau.⁴ Assuming a yield of 100 bushels per acre, 10,000 corn plants on an acre yield a dry weight of 2160 kg. of corn. The total dry weights of the plants at maturity would be about 6000 kg. After deducting 322 kg. of mineral matter there would be a residue of 5678 kg. of organic matter, of which about 2675 kg. is carbon. The glucose equivalent of this is 6678 kg. This is less than the true amount formed, since some would have been consumed in

¹ A recent review is given by W. M. Manning, *J. Phys. Chem.*, **42**, 815 (1938).

² Blum, H. F., *Am. Naturalist*, **71**, 350 (1937).

³ Stiles, W., "Photosynthesis, The Assimilation of Carbon by Green Plants," London, Longmans, Green, 1925; Spoehr, H. A., "Photosynthesis," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926; Stiles, W., *Sci. Progress*, **25**, 590 (1931); Baly, E. C. C., *Sci. J. Roy. Col. Sci.*, **2**, 58 (1932).

⁴ Transeau, E. N., *Ohio J. Sci.*, **26**, 1 (1926).

respiration during the life of the plants. This is estimated at 2045 kg. so that the total glucose made by the plants would have been 8732 kg. This is estimated to have required not far from 33 million calories of energy. The total energy of sunlight falling during this period on the acre is estimated as 2043 million calories, so that about 1.6 per cent of the light energy might have been used in photosynthesis. If it be assumed that only about 20 per cent of the incident radiant energy is in the wave-length regions capable of causing photosynthesis, then the overall efficiency of this light would be raised to about 8 per cent. There are several reasons for this low value. There are large reflection losses and some energy is lost by transmission.⁵ During a large part of the growing period, much of the energy reaches merely the ground instead of the leaves of the plants, causing a loss estimated for the period at about 54 per cent. Respiration liberates about a quarter of the energy absorbed in the photosynthetic process. Another loss is in the energy required for transpiration. For every kilogram gained in dry weight, about 276 are evaporated during the growing season.

Formaldehyde as Intermediate. Von Baeyer⁶ seems to have been the first to suggest the formation of formaldehyde in an initial stage of the process. Sabalichschka⁷ showed that certain plants, when deprived of carbon dioxide and supplied with formaldehyde, polymerize the latter to sugars and starch, even in the absence of light. From a study of the assimilatory quotient CO_2/O_2 , Willstätter and Stoll⁸ contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be one, that indicated by the equation in the first paragraph. For the formation of glycollic acid, it would be 1.33, for formic acid 2.0 and for oxalic acid 4.0. That formaldehyde under the influence of ultraviolet light of wave-lengths scarcely transmitted by glass acquires the power of reducing copper sulfate in the presence of sodium citrate or carbonate was claimed by Moore and Webster.⁹ This assumed photocondensation of formaldehyde (see Chapter 22) did not require the presence of an inorganic activator, probably proceeded at its maximum velocity when the concentration of formaldehyde was approximately 5 per cent and was aided by a slight alkalinity. Ram and Dhar¹⁰ claim to have obtained small yields of reducing sugars when aqueous formaldehyde was exposed to sunlight in the presence of ferric chloride or kieselsguhr. In the mixture of sugars (formose) which results from the polymerizing action of certain alkaline condensing agents on formaldehyde, Küster and Schoder¹¹ have identified *dl*-fructose, a ketopentose and sorbose. Ascorbic acid has been said by West and Ney¹² to be an active catalyst for the formation of reducing sugars from formaldehyde. It is unlikely that a photocondensation of formaldehyde of the type studied in *in vitro* experiments plays a significant role in the processes by which the plant forms sugars and cellulose.

Klein and Werner¹³ claim to have detected the production of formaldehyde as an intermediate in assimilation. Other aldehydes have, however, occasionally

⁵ Shull, C. A., *Science*, **67**, 107 (1928).

⁶ von Baeyer, A., *Ber.*, **3**, 68 (1870).

⁷ Sabalichschka, T., *Z. Angew. Chem.*, **5**, 684 (1922); *J. Soc. Chem. Ind.*, **42**, 65A (1923).

⁸ Willstätter, R., and Stoll, A., *Ber.*, **50**, 1777 (1917).

⁹ Moore, B., and Webster, T. A., *Proc. Roy. Soc.*, **90**, 168 (1918); *Chem. Abs.*, **12**, 1992 (1918).

¹⁰ Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.*, **14**, 151 (1937); *Chem. Abs.*, **31**, 7455 (1937).

¹¹ Küster, W., and Schoder, F., *Z. physiol. Chem.*, **141**, 110 (1924).

¹² West, E. S., and Ney, L. F., *Science*, **84**, 294 (1936).

¹³ Klein, G., and Werner, O., *Biochem. Z.*, **68**, 361 (1926).

been suggested as intermediary products in natural photosynthesis.¹⁴ Acetaldehyde has been discussed as such by Klein and Pirschle.¹⁵ Some, like Barton-Wright and Pratt¹⁶ believe the first sugar formed to be a hexose. Parkin,¹⁷ however, believes that the bulk of the hexose sugars detectable in the leaf arise as a result of the inversion of sucrose. Bodnár, Róth and Bernauer¹⁸ believe that, although in the leaves of *Tropaeolum majus*, formaldehyde gives rise to sugars, its presence inhibits the condensation of sugars to starch.

Attempts to Obtain Photosynthesis Without Chlorophyll. One attack has involved the use of ultraviolet light in the effort to duplicate *in vitro* some of the processes of photosynthesis. Since these attempts have avoided the use of the plant pigments and have employed ultraviolet light of wave-lengths far shorter than those available in sunlight, it is evident that the results can tell but little regarding the occurrences which actually take place in the plant under physiological conditions. If these attempts are viewed in the light of experiments conducted to determine the possibility of artificially producing the carbohydrates as food materials independently of the plant, they afford little hope for a practical outcome. The energy required to produce the carbohydrates which have been claimed in even the most promising of these experiments is far greater than the energy bound in the carbohydrate reaction products.

Baly and Heilbron¹⁹ claimed that detectable quantities of formaldehyde result when an aqueous solution of carbon dioxide is exposed to ultraviolet rays with agitation. The agitation was thought to decrease the local formation of hydrogen peroxide which prevented the possibility of obtaining a formaldehyde test by oxidizing that material to formic acid. In these early experiments it was believed that evidence had been advanced that wave-lengths less than 2200Å might produce one or two parts of formaldehyde in 100,000 of carbon dioxide solution in 18 to 72 hours. If wave-lengths of about 2900Å were simultaneously used, it was believed that the formaldehyde was polymerized to reducing sugars.

Similar claims had been made previously, although in these, other substances had been employed as catalysts. Moore and Webster²⁰ claimed to have detected formaldehyde when carbon dioxide solutions containing colloidal uranium oxide were exposed to sunlight, thus confirming still earlier observations of Bach²¹ and of Usher and Priestley.²² Baly and coworkers also claimed to have obtained positive results in visible light by the use of a number of the catalysts of Moore and others, although they were at one time of the opinion that these may have acted instead as internal filters capable of removing those ultraviolet rays which polymerize formaldehyde. Thus this substance might be allowed to accumulate in quantities sufficient for detection. Malachite green, methyl orange, as well as colloidal uranium compounds and ferric hydroxide were, however, believed true catalysts. Baly also emphasized the necessity of controlling the hydrogen ion concentration of the irradiated solutions by maintaining an excess of magnesium carbonate.

¹⁴ Giehel, C., *Z. Unters. Nahr. Genussm.*, **48**, 218 (1924).

¹⁵ Klein, G., and Pirschle, K., *Biochem. Z.*, **158**, 340 (1926).

¹⁶ Barton-Wright, E. C., and Pratt, M. C., *Biochem. J.*, **24**, 1210, 1217 (1930); see also Klason, P., *Svensk Kem. Tids.* **46**, 208 (1934), *Chem. Abs.*, **29**, 2576 (1935); Gordon, R. B., *Ohio J. Sci.*, **29**, 131 (1929); *Chem. Abs.*, **23**, 3951 (1929); Priestley, J. H., *New Phytol.*, **23**, 255 (1924); *Chem. Abs.*, **19**, 3291 (1925).

¹⁷ Parkin, J., *New Phytol.*, **24**, 57 (1925); *Chem. Abs.*, **20**, 3022 (1926).

¹⁸ Bodnár, J., Róth, L. E., and Bernauer, C., *Biochem. Z.*, **190**, 305 (1927); see also Kretovich, V., *Z. physiol. Chem.*, **231**, 265 (1935).

¹⁹ Baly, E. C. C., and Heilbron, I. M., *J. Soc. Chem. Ind.*, **40**, 377 (1921); Baly, E. C. C., Heilbron, I. M., and Barker, W. F., *J. Chem. Soc.*, **119**, 1025 (1921); *Nature*, **112**, 323 (1923); Baly, E. C. C., *Ind. Eng. Chem.*, **16**, 1018 (1924).

²⁰ Moore, B., and Webster, T. A., *Proc. Roy. Soc.*, **B87**, 168 (1913); **B90**, 168 (1918); *Chem. Abs.*, **12**, 1992 (1918).

²¹ Bach, A., *Compt. rend.*, **116**, 1145 (1893).

²² Usher, F. L., and Priestley, J. H., *Proc. Roy. Soc.*, **77B**, 369 (1906); **78B**, 322 (1906); Ferrous salts were believed effective by Stoklasa, J., and Zdobnický, W., *Ber.*, **50**, 1777 (1917); *Centr. Biochem. Biophys.*, **18**, 370.

Many chemists attempted without success to confirm these observations.²⁰

During this period, Baly²⁴ claimed also to have synthesized large amounts of reducing sugars by exposing aqueous 40-per cent formaldehyde solutions to the rays of the quartz mercury arc in the presence of calcium carbonate. By certain concentration methods, there was obtained a viscous syrup with sweet taste and reducing properties. An examination of this material by Irvine and Francis²⁵ showed no ketoses, polysaccharides or anhydro-sugars, but about 9.3 per cent of sugars and 80 per cent of non-sugar compounds containing hydroxyl groups.

In subsequent work, Baly, Davies, Johnson and Shanassy²⁶ concluded that the substance first formed from carbon dioxide might be some complex aldehyde other than formaldehyde. They also claimed that complex organic compounds may be synthesized by the action of ultraviolet light on suspensions of various insoluble powders, such as aluminum, barium sulfate, aluminum hydroxide, and basic carbonates of aluminum, magnesium and zinc, in water through which a stream of carbon dioxide is passed. It was thought essential that the carbon dioxide be adsorbed on these materials. The compounds produced appeared to be of the nature of complex carbohydrates. It was also believed²⁷ that the total amount of material photosynthesized at a colored surface by visible light was greater than that produced at a white surface by ultraviolet light. Nickel or cobalt carbonates were thought particularly effective, although easily poisoned.

Baur and Rebmann,²⁸ in a repetition of the Moore and Webster experiments were unable to detect formaldehyde, oxalic or glyoxalic acids. Baur and Büchi²⁹ attributed the formation of carbohydrates in experiments with dyestuffs such as malachite green to a decomposition of the dye rather than to true photosynthesis from carbon dioxide. Their observations were in general confirmed by Dean Burk,³⁰ who employed condensed sunlight. Nevertheless, the amounts of formaldehyde produced from the dye itself were very small. Amines are also produced, and under aerobic and alkaline conditions, nitrites as well.

Emerson³¹ was unable to obtain any photosynthetic effects by the use of a purified nickel carbonate preparation.

Recently, Dhar and Ram³² claimed that from 100 cc. of a 10-per cent solution of potassium carbonate mixed with one gram of powdered magnesium and in the presence of zinc oxide, gave after 5.5 hours of exposure to direct sunlight 0.0045 gram of formaldehyde, although no reducing sugar could be detected.³³ The occurrence of traces of formaldehyde in rain water was attributed to the action of light of wave-length 2550 Å, which had escaped absorption by the ozone layer. Decomposition of formaldehyde by the wave-length 2660 Å is thought to be hindered by the presence of hydrogen in the upper atmosphere.

²⁰ Spoehr, H. A., *J. Am. Chem. Soc.*, **45**, 1185 (1923); Porter, C. W., and Ramsperger, H. C., *J. Am. Chem. Soc.*, **47**, 79 (1925); Vorländer, D., *Ber.* **58B**, 2656 (1925); Reggiani, M., *Helv. Chim. Acta*, **15**, 1383 (1932); Qureshi, M., and Mohammad, S. S., *J. Phys. Chem.*, **36**, 2205 (1932); see, however, Dhar, N. R., *J. Chem. Soc.*, **124**, 1860 (1923).

²⁴ See also Pribram, R., and Franke, A., *Ber.*, **44**, 1035 (1911); *Monatsh.*, **33**, 415 (1912); Akhmatov, A. S., and Baruishanskaya-Landsberg, F. S., *J. Phys. Chem. (U.S.S.R.)*, **6**, 83 (1935); *Chem. Abs.*, **29**, 7809 (1935).

²⁵ Irvine, J. C., and Francis, G. V., *Ind. Eng. Chem.*, **16**, 1019 (1924).

²⁶ Baly, E. C. C., Davies, J. B., Johnson, M. R., and Shanassy, H., *Proc. Roy. Soc.*, **116A**, 197 (1927); see also Mezzadrolì, G., *Rev. ind. agr. Tucumán*, **19**, 154, 526 (1928); *Chem. Abs.*, **23**, 2367 (1929); Mezzadrolì, G., and Varetton, E., *Chimie et Industrie*, Special No. 778, March (1931); Mezzadrolì, G., and Gardano, G., *Atti acad. Lincei*, **6**, 160 (1927); *Chem. Abs.*, **22**, 760 (1928).

²⁷ Baly, E. C. C., Stephen, W. E., and Hood, N. R., *Proc. Roy. Soc.*, **116A**, 212 (1927); Baly, E. C. C., *Science*, **68**, 364 (1928); Baly, E. C. C., and Hood, N. R., *Proc. Roy. Soc.*, **122A**, 393 (1929).

²⁸ Baur, E., and Rebmann, A., *Helv. Chim. Acta*, **5**, 828 (1922).

²⁹ Baur, E., and Büchi, P. F., *Helv. Chim. Acta*, **6**, 959 (1923).

³⁰ Burk, D., *J. Am. Chem. Soc.*, **49**, 1819 (1927); Cf. Ram, A., [*Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 83 (1934)]; *Chem. Abs.*, **29**, 7383 (1935); Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.*, **15**, 321 (1938); *Chem. Abs.*, **32**, 8941 (1938)] for the alleged production of formaldehyde from many organic compounds by sunlight.

³¹ Emerson, R., *J. Gen. Physiol.*, **13**, 163 (1929); see also Baur, E., *Z. physik. Chem.*, **131**, 143 (1928).

³² Dhar, N. R., and Ram, A., *Nature*, **129**, 205 (1932); *Z. anorg. allgem. Chem.*, **206**, 171 (1932); Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **35**, 1418, 1424 (1931); Dhar, N. R., and Sanyal, R. P., *Ibid.*, **29**, 926 (1925).

³³ Dhar, N. R., and Ram, A., *Nature*, **132**, 819 (1933); *J. Indian Chem. Soc.*, **10**, 287 (1933); *Trans. Faraday Soc.*, **30**, 142 (1934); *Nature*, **131**, 800 (1933); *J. Phys. Chem.*, **37**, 525 (1933); Gore, V., *Ibid.*, **39**, 399 (1933).

According to Rajvansi and Dhar,⁸⁴ the most effective catalysts for the formation of formaldehyde from carbon dioxide solution in sunlight are manganous chloride and cobalt carbonate, with which a yield of formaldehyde of the order of 0.0005 per cent by volume was claimed. When nascent carbon dioxide was prepared from barium carbonate and hydrogen chloride, formaldehyde was produced by light even in the absence of a photosensitizer. The temperature coefficient of sugar formation in sunlight from a 3-per cent aqueous solution of formaldehyde was found to be 1.2 between 30 and 40°C.

Gore⁸⁵ finds that mixtures of tartaric acid and various aldehydes or alcohols in aqueous solutions after exposures to sunlight of 84 or 100 hours without photosensitizers gave positive sugar tests with Benedict's solution. This did not occur in darkness. Gore assumes that light aids the decomposition of tartaric acid by aldehyde to produce nascent carbon dioxide, which reacts with water to produce formaldehyde which polymerizes with the formation of the sugars. It is assumed that when alcohols are used they are first oxidized to aldehydes by light.

Notwithstanding the poor yields that have been reported in all such investigations, Roman⁸⁶ patented the production of hexoses and higher carbohydrates by the polymerization of aldehydes, particularly formaldehyde, by light, preferably orange-red. The reaction is said to be best effected in the presence of a compound capable of combining with the carbohydrate, such as an alkaline-earth hydroxide.

In subsequent work, Baly⁸⁷ turned to the use of catalysts of ferric oxide supported on kieselguhr previously coated with alumina. The activity was said to be increased by the addition of small quantities of thorium dioxide to the ferric oxide. Bell⁸⁸ was unable to confirm these results. Further negative results in the photosynthesis of formaldehyde were also reported by Konstantinova-Shlezinger,⁸⁹ and Zscheile⁴⁰ reported forty futile attempts to repeat the experiments of Baly with visible light and nickel and cobalt carbonates. He felt that Baly's use of cylinder carbon dioxide may have been a source of organic impurities. Dhar, Rao and Ram⁴¹ claimed success with the use of nickel carbonate and colloidal ferric hydroxide in 2-per cent sodium bicarbonate solutions, notwithstanding Baly's insistence that the catalyst be free from alkali. MacKinney⁴² obtained completely negative results with these slightly alkaline catalysts in sunlight or with ultraviolet light between 2900 and 3000Å.

Yajnik and Trehana⁴³ claimed to have verified some of the observations of Baly. White catalysts gave no yield unless artificially colored. The best results were claimed for green, red and blue catalysts, copper arsenate being the most efficient of those tested. Baly⁴⁴ recently maintained that it is essential for success that there be a surface which is a true crystal lattice of nickel oxide.

THE PHYSIOLOGICAL MECHANISM

Green leaves absorb from 50 to 60 per cent of the incident infrared and approximately 90 per cent of the ultraviolet rays, according to Seybold.⁴⁵ In the red region, the maximum absorption by leaves occurs at 6700Å. That of an acetone extract of chlorophyll occurs at 6500Å. There is a second maximum in the blue-violet, and transmission is greatest in the green. In the living leaf

⁸⁴ Rajvansi, A. R., and Dhar, N. R., *J. Phys. Chem.*, **36**, 567, 575 (1932).

⁸⁵ Gore, V., *J. Phys. Chem.*, **37**, 745 (1933).

⁸⁶ Roman, L. H., German P. 590,236, Jan. 4, 1934; *Chem. Abs.*, **28**, 2013 (1934); Carboxyhyd. A.-G. British P. 374,044 and 458,359.

⁸⁷ Baly, E. C. C., *Nature*, **126**, 666 (1930); *Trans. Faraday Soc.*, **27**, 545 (1931).

⁸⁸ Bell, J., *Trans. Faraday Soc.*, **27**, 771 (1931).

⁸⁹ Konstantinova-Shlezinger, M., *J. Phys. Chem., U.S.S.R.*, **2**, 780 (1931); *Chem. Abs.*, **27**, 5374 (1933).

⁴⁰ Zscheile, F. P. Jr., *J. Am. Chem. Soc.*, **54**, 973 (1932).

⁴¹ Dhar, N. R., Rao, G. G., and Ram, A., *Trans. Faraday Soc.*, **27**, 554 (1931); Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **35**, 1418 (1931).

⁴² MacKinney, G., *J. Am. Chem. Soc.*, **54**, 1688 (1932).

⁴³ Yajnik, N. A., and Trehana, F. C., *J. chim. phys.*, **28**, 517 (1931).

⁴⁴ Baly, E. C. C., *Nature*, **140**, 930 (1937). See also Ostrikov, M. S., *Acta Univ. Voronegiensis*, No. 3, 95 (1937); *Chem. Abs.*, **32**, 6949 (1938).

⁴⁵ Seybold, A., *Planta (Abt. E, Z. wiss. Biol.)*, **21**, 251 (1933); *Chem. Abs.*, **28**, 3758 (1934).

the chlorophyll spectrum is displaced somewhat toward the infrared as compared with that which it exhibits in solution.

Although the carotenes and xanthophyll also make contributions to the absorption of visible light by the leaf, the absorption of chlorophyll is the predominant cause of the color of the leaf.⁴⁶

That chlorophyll may be separated into fractions was suggested by early observers, and confirmed by Willstätter and Stoll.⁴⁷ They showed that there are two green pigments chlorophyll-*a* and chlorophyll-*b* present in all plant leaves and separable by a preferential solubility of chlorophyll-*a* in petroleum ether and of chlorophyll-*b* in 90-per cent methanol. In the higher plants there is about three times as much of the former as of the latter.⁴⁸

Wlodek⁴⁹ noted that the stripes of the first absorption band, corresponding to both chlorophyll-*a* and *b*, alter in width during exposure of the leaf to light. This indicates either a change in the relative amounts of the two forms of chlorophyll or the appearance of a new type of spectrum due to unstable compounds of chlorophyll with carbon dioxide. Shifts in the situation of the absorption bands of chlorophyll in the presence of certain hydrophilic and lipophilic materials are considered to support a granular model of the chloroplastid by Wakkie.⁵⁰

Action of Light on Chlorophyll. Crude chlorophyll in alcoholic solution was not decomposed by the action of ultraviolet rays in exposures of five to sixty minutes. Bierry and des Bancel⁵¹ found that on prolonged exposures to two mercury arcs, the solutions became faintly yellow and gave positive tests for urobilinogen. A benzene solution of chlorophyll became colorless under these conditions but did not show the color reactions of urobilinogen.⁵² According to Dangeard,⁵³ when light is allowed to fall on a mixture of chlorophyll and Pinaverdol, the former is decolorized. The latter is also attacked and finally destroyed by the light absorbed, not by itself, but by the chlorophyll. It was suggested that the carotene and xanthophylls which accompany chlorophyll in the leaf might also be similarly bleached by the photosensitizing action of chlorophyll.

Bleaching of chlorophyll occurs in the presence of oxygen and of such acceptors as diethylallyl- and diallylthiocarbamide, according to Weber.⁵⁴ Ferrous sulfate is also active in neutral or feebly acid solution. In the absence of an acceptor the rate of bleaching is slow. It increases rapidly in the presence of small amounts of acceptor, attains a maximum and diminishes logarithmically with increasing acceptor concentrations. In all cases there is a marked induction period. The rate of bleaching is but little affected by temperature. The bleaching is greatly inhibited by certain phenols, quinones and amines. It is suggested that

⁴⁶ The chemistry of chlorophyll has recently been reviewed by Steele, C. C., *Chem. Rev.*, 20, 1 (1937) and by Fischer, H., *Chem. Rev.*, 20, 41 (1937).

⁴⁷ Willstätter, R., and Stoll, A., "Untersuchungen über Chlorophyll," Berlin, 1913; transl. by Scherz, F., and Merz, A., Science Publishing Co., 1928.

⁴⁸ Their photosynthetic functions have been reviewed by Spoehr, H. A., *Annual Rev. Biochem.*, 2, 453 (1933) and by Stoll, A., *Naturewiss.*, 24, 53 (1936).

⁴⁹ Wlodek, J., *Bull. Internat. Acad. Pol. Sci. Lettres B*, 407 (1924); *Chem. Abs.*, 19, 2687 (1925).

⁵⁰ Wakkie, J. G., *Proc. Acad. Sci. Amsterdam*, 38, 1082 (1935); *Chem. Abs.*, 30, 3024 (1936). Methods for measuring the absorption of radiation by leaves are discussed by Mestre, H., *Cold Spring Harbor Symposia Quant. Biol.*, 3, 191 (1935).

⁵¹ Bierry, H., and des Bancel, J., *Compt. rend.*, 153, 124 (1911); *J. Chem. Soc.*, 100, 735 (1911).

⁵² See, however, Gouzon, B., *Compt. rend.*, 196, 1542 (1933).

⁵³ Dangeard, P. A., *Compt. rend.*, 156, 1844 (1913).

⁵⁴ Weber, K., *Ber.*, 69B, 1026 (1936); *Nature*, 137, 870 (1936); Weiss, J., *Nature*, 136, 794 (1935).

on absorption of a photon a molecule of chlorophyll is so activated as to enable it to combine with a molecule of oxygen, forming a peroxide which then oxidizes the chlorophyll. Induction and after effects are attributed to the long life-periods of the intermediate peroxide. With high acceptor concentrations, chlorophyll is stabilized by the reaction: $AO_2 + A \rightarrow 2AO$. According to Porret and Rabinowitsch, the reversible bleaching of chlorophyll is proportional to the square root of the light intensity. It is increased by formic acid and suppressed by ferrous chloride.⁵⁵

An ethylchlorophyllide solution can be reversibly oxidized by ferric chloride to a yellow unstable intermediary product from which the green solution can be regenerated by reduction with ferrous chloride. The oxidation is greatly favored by illumination.⁵⁶

Hubert⁵⁷ notes the possibility of the photodecomposition of chlorophyll during the measurement of its absorption spectrum. Suspensoid particles prepared by injecting an acetone solution of chlorophyll into water bear a negative charge which becomes positive after several hours of exposure to light, owing to photooxidation.⁵⁸ Electrical measurements made with metallic plates coated with chlorophyll and illuminated showed in experiments of Dixon and Poole,⁵⁹ that the wave-lengths which are effective in photosynthesis are unable to expel electrons from chlorophyll.

Kögel⁶⁰ attributes the photosensitivity of chlorophyll to keto-groups. Roffo⁶¹ finds pure chlorophyll strongly photoactive, a property not shared by xanthophyll, phytosterol, carotene or chlorophyllin.

When a hydrazone of phylloerythrin is exposed to light, its spectrum changes to that of phylloerythrin.⁶² Etioporphyrin, exposed to sunlight in the presence of oxygen, forms ethylmethylemaleimide, according to Deželić.⁶³

Relation of Chlorophyll to Photosynthesis. The importance of chlorophyll in the photosynthetic process is based upon the agreement between the absorption spectrum of chlorophyll and the effective wave-length regions, and also upon the approximate correlation between the photosynthetic activity of partly etiolated plants and their chlorophyll content. The latter agreement is, however, far from an exact one, so it has been suggested that other internal factors may be involved.⁶⁴ Studies at various points in the variegated leaves of *Pelargonium* by Chapman and Camp⁶⁵ revealed that no starch is produced in the non-green parts.

Attempts to reproduce the photosynthetic process *in vitro* by the use of extracts of chlorophyll have not yielded promising results. Osterhout⁶⁶ sprinkled a carbon tetrachloride solution of chlorophyll on filter paper in amounts sufficient to give it a deep green color. The treated paper was placed in airtight bell jars with large petri dishes containing 5 cc. of water. Some of the sheets were kept

⁵⁵ Porret, D., and Rabinowitsch, E., *Nature*, **140**, 321 (1937).

⁵⁶ Rabinowitsch, E., and Weiss, J., *Nature*, **138**, 1098 (1936).

⁵⁷ Hubert, B., *Proc. Acad. Sci. Amsterdam*, **37**, 684 (1934); *Chem. Abs.*, **29**, 1844 (1935).

⁵⁸ Bakker, H. A., *Proc. Acad. Sci. Amsterdam*, **37**, 688 (1934); *Chem. Abs.*, **29**, 1844 (1935).

⁵⁹ Dixon, H. H., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.*, **16**, 63 (1920); *J. Chem. Soc.*, **118**, II, 343 (1920).

⁶⁰ Kögel, G., *Strahlentherapie*, **45**, 587 (1932); *Chem. Abs.*, **27**, 2721 (1933).

⁶¹ Roffo, A. H., *Bol. inst. med. exper. cancer Buenos Aires*, **8**, 68 (1931); *Chem. Abs.*, **26**, 5125 (1932).

⁶² Fischer, H., Moldenhauer, O., and Süss, O., *Annalen*, **485**, 1 (1931); *Chem. Abs.*, **25**, 1835 (1931).

⁶³ Deželić, M., *Bull. soc. chim. roy. Yougoslav*, **6**, 11 (1935); *Chem. Abs.*, **29**, 7998 (1935).

⁶⁴ Briggs, G. E., *Proc. Roy. Soc.*, **91B**, 249 (1920).

⁶⁵ Chapman, A. G., and Camp, W. H., *Ohio J. Sci.*, **32**, 197 (1932); *Chem. Abs.*, **26**, 4629 (1932).

⁶⁶ Osterhout, W. J. V., *Am. J. Botany*, **5**, 105, 511 (1918); Osterhout, W. J. V., and Haas, A. R. S., *Science*, **47**, 420 (1918).

in darkness and others were placed in light for several days until the chlorophyll had bleached to a pale green color. The water in the dishes kept in darkness gave negative aldehyde tests and that in those in the light gave positive tests. Aniline dyes were believed to behave similarly. Baur⁶⁷ embedded the chlorophyll in collodion with an oxidation-reduction system such as methylene blue or iron salts and exposed the layer in water to sunlight. Small quantities of formaldehyde could be detected even when the water had been freed from carbon dioxide. The presence of carotene increases the yield. Dolk and van Veen⁶⁸ were unable to reduce carbon dioxide by a protein-containing chlorophyll solution, a reaction previously reported by v. Eisler and Portheim.⁶⁹

In the case of *Pinus Strobus* and *Picea excelsa*, Burns⁷⁰ finds wave-length limits for photosynthesis to be 7400 to 4500A approximately. Ursprung⁷¹ found starch formation possible between 7600 and 3300A. Both the red and the blue-violet regions are regarded as necessary for normal photosynthetic activity by Dastur and Mehta.⁷² On the basis of equal incident energies at various wave-lengths, Hoover⁷³ found the entire visible spectrum between 7200-7500A and less than 3650A to be effective. A principal maximum occurred at 6550A in the red and a secondary one at 4400A in the blue. Greater reflection and transmission in the green diminished the effectiveness of these rays. Harder, Döring and Simonis suggest that the assimilatory apparatus of green plants may be able to adapt itself to the wave-length of light in which it is grown.⁷⁴

A new type of starch formation under the influence of wave-lengths shorter than 3000A has been discussed by Richter,⁷⁵ who postulates the existence of a chlorophyllase in the leaf to account for his results.

The Mode of Action of Chlorophyll in Photosynthesis. The investigation of the mechanism of the reaction is unfortunately complicated by the necessity for studying it as it occurs in living tissues. Fundamental investigations of the process in leaves were made by Blackman⁷⁶ in 1905. These led to a recognition that the rate of the process as conducted under different conditions may be limited by different factors.

Thus, Hoover, Johnston and Brackett⁷⁷ find that in wheat, carbon dioxide limits the rate when high light intensities are used, although under conditions of high carbon dioxide concentration, light becomes the limiting factor. In an extensive transition range, both factors may be limiting, in consequence of the wide variation in the illumination and carbon dioxide concentration available for different chloroplasts. Blackman had also called attention to the influence of temperature in altering the nature of the photo-

⁶⁷ Baur, E., *Helv. Chim. Acta*, **18**, 1157 (1935); **20**, 387, 391, 398 (1937).

⁶⁸ Dolk, H. E., and van Veen, A. G., *Biochem. Z.*, **185**, 165 (1927).

⁶⁹ v. Eisler, M., and Portheim, L., *Biochem. Z.*, **135**, 293 (1923).

⁷⁰ Burns, G. R., *Science*, **78**, 130 (1933); *Plant Physiol.*, **8**, 247 (1933); **9**, 645 (1934); *J. Am. Chem. Soc.*, **59**, 944 (1937); *Am. J. Botany*, **24**, 257 (1937); *Vt. Agr. Expt. Sta. Bull.*, **402**, 2 (1936); *Chem. Abs.*, **31**, 4699, 5020 (1937); *Am. J. Botany*, **25**, 166 (1938).

⁷¹ Ursprung, A., *Ber. deut. botan. Ges.*, **35**, 44 (1917).

⁷² Dastur, R. H., and Mehta, R. J., *Ann. Botan.*, **49**, 809 (1935); *Chem. Abs.*, **30**, 503 (1936); see also Dastur, R. H., and Samant, K. M., *Ann. Botan.*, **47**, 295 (1933); *Chem. Abs.*, **27**, 4270 (1933); Dastur, R. H., and Solomon, S., *Ann. Botan.*, **1**, 147 (1937); *Chem. Abs.*, **31**, 2639 (1937).

⁷³ Hoover, W. H., *Smithsonian Inst. Miscellaneous Collections*, **95**, No. 21 (1937). No increased action due to the joint action of all wave-lengths of white light over that due to the sum of their individual effects occurs, according to Montfort, C., *Ber. deutsch. botan. Ges.*, **55**, 142 (1937); *Chem. Abs.*, **31**, 7089 (1937). An opposite result is noted by Danilov, A. N., *Arch. sci. biol. (U.S.S.R.)*, **43**, Nos. 2-3, 365 (1936); *Chem. Abs.*, **32**, 6694 (1938).

⁷⁴ Harder, R., Döring, B., and Simonis, W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse Fach Gruppe*, **VI**, 2, 129 (1936); *Chem. Abs.*, **32**, 7958 (1938).

⁷⁵ Richter, O., *Sitzber. Akad. Wiss. Wien, Math. naturw. Kl.*, **I**, 144, 157 (1935); *Chem. Abs.*, **31**, 3762 (1937).

⁷⁶ Blackman, F. F., *Proc. Roy. Soc.*, **76B**, 402 (1905); *Ann. Botan.*, **19**, 28 (1905).

⁷⁷ Hoover, W. H., Johnston, E. S., and Brackett, F. S., *Smithsonian Miscellaneous Collections*, **87**, 16 (1933); see also Smith, E. L., *J. Gen. Physiol.*, **22**, 21 (1938).

synthetic processes.⁷⁸ The temperature of the leaf also alters transpiration, and changes the state of the plasma, alters the ease of penetration of the gases and may have other effects. Furthermore, respiration is also occurring and its effects upon the results require consideration. Dhar⁷⁹ suggests that an increase in temperature may affect the respiration more than the photosynthetic process. Another complicating factor is the possibility of the existence of enzymes, which may in some manner be concerned in the process.⁸⁰ Various methods of killing leaves affect the photosynthetic process about as do various methods of inactivating enzymes. Inman⁸¹ believes some light-sensitive substance contributes to the production of free oxygen in living but not in dead, plant cell tissues. It is inactivated by trypsin, but not by pepsin, erepsin, amylopsin, diastase, urease or papain. The maximum evolution of oxygen is obtained between pH 5 and 6. The critical temperature for its evolution is 55°C, regardless of pH; that for catalase is 70°C. Wurmser⁸² directed attention to the influence of alterations of the cellular reduction potential upon the process. Rhythms in the production and disappearance of starch during 24-hour periods have been observed by Stănescu,⁸³ who followed quantitatively the variations in the products in the leaves of green plants during the course of a day. The water content of the leaves also exerts a great influence upon the rate of the process.⁸⁴ Wood⁸⁵ showed that the injection of water into a cherry-laurel leaf lowers its rate of assimilation until nearly all the injected water has disappeared from the intercellular spaces. Dehydration of the leaf by a dry wind⁸⁶ retards photosynthesis. Still another factor is the amount of carbohydrate already present.⁸⁷

To avoid so far as possible these many complicating factors some of the investigations which have proved most significant in the interpretation of the mechanism of the process have been conducted on the algae. Warburg and Negelein⁸⁸ made a series of observations of the energy exchange in the stems of *Chlorella* using light of four spectral regions. In general the reaction yield decreased with decreasing wave-length, but no relation could be discerned between the yield and the absorption coefficients. The yield in the red, a region of high absorption, was greater than that in the green, a region of very weak absorption, but the yield in the latter case was greater than that in the blue, the region of strongest absorption. The decomposition in the ultraviolet and in the region between 7000 and 7800Å could not be accurately determined. There was no utilization of carbon dioxide under the influence of light in the infrared. In *Ulva lactuca*, the yield for equal incident intensities was a maximum in the region in which the chlorophyll absorption was least, according to Wurmser.⁸⁹

Warburg recognized the need for the absorption of several quanta per molecule in order to secure enough energy for the reaction to proceed. The results indicated that four quanta of red or yellow light or five of blue light were required for

⁷⁸ Chesnokov, V., and Bazurina, E. N., *Compt. rend. acad. sci. U.R.S.S.*, **8**, 193 (1930A); *Chem. Abs.*, **25**, 313, 2457 (1931). A review in Russian is given by Nekrasov, N. I., and Krashen-nikov, F. N., *Uspekhi Khim.*, **6**, 334 (1937).

⁷⁹ Dhar, N. R., *J. Indian Chem. Soc.*, **10**, 541 (1933); *Chem. Abs.*, **28**, 2293 (1934); Singh, B. N., and Kumar, K., [*Proc. Indian Acad. Sci.*, **1B**, 736 (1935); *Chem. Abs.*, **29**, 6277 (1935)] consider the effects of temperature on the process in radish leaves.

⁸⁰ Molisch, H., cited by Stiles, W., *Scientia*, **41**, 122 (1927); Molisch, H., *Z. Botan.*, **17**, 577 (1925).

⁸¹ Inman, O. L., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 184 (1935); *Chem. Abs.*, **30**, 7627 (1936).

⁸² Wurmser, R., *Compt. rend. soc. biol.*, **95**, 1237 (1926).

⁸³ Stănescu, P. P., *Ann. Sci. Univ. Jassy*, **14**, 383 (1927); *Chem. Abs.*, **22**, 2390 (1928).

⁸⁴ Dastur, R. H., *Ann. Botan.*, **39**, 769 (1925).

⁸⁵ Wood, J. G., *Australian J. Exp. Biol.*, **6**, 127 (1929); *Chem. Abs.*, **24**, 1882 (1930).

⁸⁶ Skvortzov, S. S., *Bull. Applied Bot., Gen. Plant Breeding, Leningrad*, **25**, No. 3, 45 (1931); *Chem. Abs.*, **26**, 5605 (1932).

⁸⁷ Kursanov, A. L., *Planta, Abt. F. Z. wiss. Biol.*, **20**, 535 (1933); *Chem. Abs.*, **28**, 2750 (1934); Spoehr, H. A., and Long, F. L., *Carnegie Inst. Washington, Yearbook*, **17**, 60 (1918); Lyubimenko, V. N., *Rev. Gen. Botan.*, **40**, 415, 486 (1928); *Chem. Abs.*, **23**, 412 (1929).

⁸⁸ Warburg, O., and Negelein, E., *Z. physik. Chem.*, **106**, 191 (1923).

⁸⁹ Wurmser, R., *Compt. rend.*, **177**, 644 (1923); *J. Phys. Radium*, **7**, 33 (1926). The work indicated that Einstein's law did not directly account for the photosynthetic behavior of this sea-weed.

the decomposition of a molecule of carbon dioxide. When corrections were made for the light absorbed by the other photochemically inactive pigments present, it was found that more than three and less than five quanta of blue light were required per molecule of carbon dioxide. The energy efficiency of the total reaction, obtained by dividing 112 kcal. by four times the equivalent energy of the light employed, was found to be 65 per cent for 6600Å, 57 per cent for 5780Å and 43 per cent for 4360Å.

It was also shown in later experiments conducted at very high and at very low light intensities that it is possible to distinguish between the photochemical reaction with low temperature coefficient and a subsequent reaction, called by Warburg the Blackman reaction. This has a higher temperature coefficient and is a thermal reaction.⁹⁰ For a given wave-length, the specific photochemical reaction is greater the smaller the intensity, and with very low intensities the action is proportional to the intensity.

Narcotics, such as 0.5×10^{-4} molar phenylurethane, powerfully inhibited both the photochemical and the Blackman reactions. Hydrogen cyanide and hydrogen sulfide, however, inhibited only the Blackman reaction.

Considerable information has been yielded by studies of the effect of intermittent light. By using a rotating sector, Brown and Escombe⁹¹ found that three-quarters of the light from a given source could be cut out in each revolution of the sector without decreasing the rate of photosynthesis by leaves. Willstätter attributed this to the slowness of the diffusion of carbon dioxide to the cells during the dark period. In Warburg's experiments with light of high intensity and with a high concentration of carbon dioxide, it was found that even in algae, a given amount of light reduced more carbon dioxide when applied intermittently than when the illumination was continuous. The increase in the yield depended upon the frequency of the flashing. It was 10 per cent with four periods per minute and 100 per cent with a frequency of 8000 per minute. Emerson and Arnold⁹² believed that certain steps in the Blackman reaction proceed during the dark period. When the light intensity is high, the initial photochemical reaction is capable of proceeding at great speed. In continuous light, however, it can go no faster than the Blackman reaction. Since it seemed likely that in the latter, chlorophyll is regenerated, it may be that the Blackman reaction limits the rate of the photochemical process. Higher efficiency of utilization of the light would be obtained if each flash lasted only long enough to build up the equilibrium concentration of intermediate products and each dark period were long enough to allow the slower Blackman reaction time to use up all the intermediate products present at the end of the light period. By using only fifty flashes per second and making the flashes much shorter than the dark periods, Emerson and Arnold were able to increase the yield by 300 to 400 per cent of that under continuous illumination. The necessary dark period varied from about 0.03 to 0.4 second, depending on the temperature. The light period could be reduced to 0.00001 second. The light reaction is dependent upon the carbon dioxide concentration and is inhibited by narcotics. They differed from Warburg in not finding the dark reaction inhibited by narcotics, although it is inhibited by cyanides. It is independent of the carbon dioxide concentration. From the speed of the light reaction, it was suggested that a chlorophyll-carbon dioxide complex may be activated to form molecules capable of undergoing the Blackman reaction.

⁹⁰ Warburg, O., *Biochem. Z.*, **166**, 386 (1925); **100**, 230 (1919); **103**, 188 (1920).

⁹¹ Brown, H. T., and Escombe, F., *Proc. Roy. Soc.*, **76B**, 29 (1905). For reviews, see Briggs, G. E., *Biol. Review Cambridge Phil. Soc.*, **10**, 460 (1935); Emerson, R., *Enzymforsch.*, **5**, 305 (1936).

⁹² Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **15**, 391 (1931-2); **12**, 623 (1929). There is no similarity between the Blackman reaction and the decomposition of hydrogen peroxide by *Chlorella*, according to Emerson, R., and Green, L., *Plant Physiol.*, **12**, 537 (1937).

From studies on several higher plants, Briggs⁹⁸ concluded that, contrary to the results of Warburg and Negelein, the number of quanta required for the production of a molecule of carbon dioxide increases discontinuously with increasing wave-length. In the case of spruce, Burns⁹⁴ found the relative number of quanta required per molecule of carbon dioxide to be 9.5, 10 and 5 for the wave-length regions 7200-6300A, 7200-5600A and 4700-3900A. Thus the quantum yields were much smaller than those found by Warburg. Recently, Manning, Stauffer, Duggar and Daniels⁹⁵ reported that an extensive series of investigations had failed to confirm the quantum yield for *Chlorella* reported by Warburg as 0.25. Instead, the value was much lower, 0.05, and in some experiments, particularly those with higher light intensities, was still lower, even approximating zero. No explanation of the discrepancy could be advanced. It was pointed out that the Warburg results indicated a high enough efficiency in the utilization of the energy⁹⁶ for it to be profitable to attempt formulations of the mechanism of the coupled reactions which occur. The newer low quantum yields, however, make possible a large number of conceivable mechanisms, and leave our knowledge of the nature of this fundamental reaction in a chaotic state. Only a brief discussion will, therefore, be given of a few of the mechanisms which have been suggested.⁹⁷

The mechanism suggested by Willstätter and Stoll was based upon their belief that carbon dioxide reacts with chlorophyll-*a* to form a carbon dioxide-chlorophyll complex of the same color as chlorophyll.⁹⁸ The absorption of light was thought to convert this into an isomer of peroxide-like nature. This is capable of liberating oxygen and an oxymethylene group with regeneration of chlorophyll.⁹⁹ Several observations by Warburg lent support to this theory. *Chlorella* in 0.03 molar hydrogen peroxide solution in darkness evolved the same amount of oxygen as does the same amount of the irradiated algae in the Blackman reaction. The effects of temperature, hydrogen cyanide and narcotics on the Blackman reaction and the evolution of oxygen from hydrogen peroxide by *Chlorella* were similar.

Photosynthesis occurs in the absence of oxygen in at least 14 species of marine algae. Within a second of the illumination, oxygen is liberated and may be detected by its action on luminous bacteria.¹⁰⁰ This is confirmed by Gaffron.¹⁰¹ Carbon monoxide influences the process, possibly by an action on an enzyme assumed to control the liberation of oxygen in the Blackman reaction. Kohn¹⁰² finds that iodoacetic acid and its amide inhibit photosynthesis by attacking the Blackman reaction.

Ostwald¹⁰³ suggested the possibility of a primary photoactivation to a lipid peroxide at an interface between lipid and protein, the assumed reaction being in some manner promoted by chlorophyll, which was not thought to enter directly into the mechanism.

⁹⁸ Briggs, G. E., *Proc. Roy. Soc.*, 105B, 1 (1929); *Brit. Chem. Abs.* A, 960 (1929).

⁹⁴ Burns, G. R., *Plant Physiol.*, 8, 247 (1933); *Chem. Abs.*, 27, 3239 (1933).

⁹⁵ Manning, W. M., Stauffer, J. F., Duggar, B. M., and Daniels, F., *J. Am. Chem. Soc.*, 60, 266 (1938); Manning, W. M., Juday, C., and Wolf, M., *ibid.*, 274; *Trans. Wis. Acad. Sci.* 31, 377 (1938).

⁹⁶ Adams, E. Q., interprets the results as indicating an efficiency of 98.6 per cent [*J. Am. Chem. Soc.*, 48, 292 (1926)] if the fundamental reaction is assumed to be $\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{HCHO} + 2\text{H}_2\text{O}_2$.

⁹⁷ Prelltcker, K., *Biochem. Z.*, 199, 12 (1928) applied stereochemical ideas to the theory of photosynthesis.

⁹⁸ Willstätter, R., and Stoll, A., *Ber.*, 50, 1791 (1917); see also Peklo, J., *Chem. News*, 129, 90 (1924).

⁹⁹ An earlier theory of Willstätter, since discarded, assumed a participation of xanthophyll and carotene. See also Heilbron, I. M., *J. Soc. Chem. Ind.*, 43, 89T (1924); *Chem. Abs.*, 15, 3072 (1921).

¹⁰⁰ Harvey, E. N., *Plant Physiol.*, 3, 85 (1928); *Chem. Abs.*, 23, 185 (1929).

¹⁰¹ Gaffron, H., *Biochem. Z.*, 280, 337 (1935).

¹⁰² Kohn, H. I., *J. Gen. Physiol.*, 19, 23 (1935).

¹⁰³ Ostwald, Wo., *Kolloid Z.*, 33, 356 (1923).

Attention was also devoted to the possibility that light enables the chlorophyll in some manner to split hydrogen from water, producing hydrogen peroxide. Thunberg¹⁰⁴ suggested that hydrogen, carbon dioxide and water might react to produce oxygen and H_2CO_2 , the latter breaking down to formaldehyde and water. Weigert¹⁰⁵ suggested that in an internal photoelectric effect in a chlorophyll-water complex, the passage of an electron from the pigment to the water with the production of a hydrogen atom and hydroxyl ion may occur. Two hydroxyl ions might then form hydrogen peroxide, returning the electrons to chlorophyll molecules.

Shibata and Yakushiji¹⁰⁶ suggest that the chlorophyll-carbonic acid complex binds four water molecules coordinatively to the magnesium atom. The absorption of four quanta activates the water molecules of the complex forming four hydrogen atoms and four hydroxyl groups. The hydrogen atoms react with carbonic acid with the formation of formaldehyde and two molecules of water. The four hydroxyl radicals form two molecules of hydrogen peroxide which are subsequently decomposed to water and oxygen by the leaf catalase. The catalase poison, hydroxylamine, added in low concentrations, inhibits the liberation of oxygen and changes assimilation into respiration. This theory was developed particularly to account for the now disputed quantum yield of 0.25.

Kögel¹⁰⁷ believed that chlorophyll activates the carbon dioxide and forms $(\text{OH})_2\text{C}(\text{OH})_2$ as the initial product.

Kautsky and Hirsch¹⁰⁸ studied the changes in the fluorescence of chlorophyll in leaves during exposure to light. The intensity of the fluorescence rises rapidly to a maximum (one second) and then slowly drops (four minutes) to a low value, which thereafter remains constant. At 0°C ., or after the addition of hydrogen cyanide, the initial rise still occurs but there is no subsequent decrease. It is suggested that the period of falling fluorescence intensity represents an induction period during which the Blackman reaction occurs. Normal assimilation is assumed to occur on the final weak fluorescent level of the curve for the fluorescence intensity at various times during irradiation. The steep initial rise in the curve, which is independent of temperature or cyanide, increases with the light intensity. It is ascribed to the establishment of the photochemical equilibrium:

$\text{Chlorophyll-CO}_2 + h\nu \rightleftharpoons \text{Chlorophyll-formaldehyde peroxide}$. The fluorescence is largely inhibited by oxygen.¹⁰⁹ The absorption of a quantum by the pigment system¹¹⁰ activates it so that it fluoresces intensely. The fluorescence may then be quenched by the transfer of the excitation energy to an unidentified compound containing loosely bound molecular oxygen, designated $\text{A}(\text{O}_2)$. This energy (about 37 kcal. or a little less than the red fluorescence, 42 kcal.) stabilizes the oxygen compound. The energy-transfer is a surface phenomenon, which can be abolished by such a surface-active substance as phenylurethane. The stable excited oxygen compound is changed back to the dissociable one in the chloroplasts by a

¹⁰⁴ Thunberg, T., *Z. Physik. Chem.*, **106**, 305 (1923). A substance liberating iodine from potassium iodide is said to be formed when leaves of sugar cane (also stalks and roots) are exposed to sunlight. Fujii, M., and Nishioeda, M., *Rept. Gov. Sugar Expt. Sta., Tainan, Formosa*, No. 5, 47 (1938); *Chem. Abs.*, **32**, 8487 (1938).

¹⁰⁵ Weigert, F., *Z. physik. Chem.*, **106**, 313 (1923).

¹⁰⁶ Shibata, K., and Yakushiji, E., *Naturwiss.*, **21**, 267 (1933); Yakushiji, E., *Acta Phytochem.*, **7**, 93 (1933); *Chem. Abs.*, **27**, 4269 (1933).

¹⁰⁷ Kögel, G., *Naturwiss.*, **19**, 571 (1931).

¹⁰⁸ Kautsky, H., and Hirsch, A., *Naturwiss.*, **19**, 964 (1931); Kautsky, H., and Spohn, H., *Biochem. Z.*, **274**, 435 (1934); **277**, 250 (1935).

¹⁰⁹ Kautsky, H., Hirsch, A., and Davidsohn, F., *Ber.*, **65**, 1762 (1932); *Chem. Abs.*, **27**, 1029 (1933). Dastur, R. H., and Desai, B. L., [*Annal. Botan.*, **47**, 69 (1933)] interpret the curves for fluorescence on the basis of a double photo-reaction involving, first the activation of carbon dioxide and second, the decomposition of water.

¹¹⁰ Kautsky, H., and Hirsch, A., *Biochem. Z.*, **274**, 423 (1934). For recent studies of fluorescence in *Chlorella*, see Wassink, E. C., Vermeulen, D., Reman, G. H., and Katz, E., *Enzymologia*, **5**, 100, 110 (1938).

heavy metal catalyst, liberating oxygen, energy and the substance A. The latter again combines with molecular oxygen. It is this reaction which depends upon temperature and which is inhibited by cyanides. The energy liberated in the breakdown of the oxygen compound is utilized in the reduction of carbon dioxide.

That the dehydrogenation of chlorophyll may play a part in the photosynthetic process was suggested by Conant, Dietz and Kamerling.¹¹¹ In a dark enzymatic process, six molecules of carbon dioxide may remove two hydrogen atoms from each of twelve chlorophyll molecules forming a hexose, six molecules of water and twelve of dehydrochlorophyll. In a subsequent photochemical reaction, chlorophyll is regenerated by abstracting hydrogen from water, releasing its oxygen.

On the basis of some observations by Stoll,¹¹² Willstätter¹¹³ altered the Conant concept of the process. In place of assuming that the hydrogen atoms of chlorophyll are lost as a pair in its dehydrogenation, he considered them to transfer separately, monodehydrochlorophyll thus acting as an intermediary compound. It is formed by the action of an oxygen molecule upon chlorophyll and is converted into dehydrochlorophyll by the transfer of its hydrogen atom to the magnesium carbonic acid complex. Then, in light, the dehydrochlorophyll, acting with water, reforms monodehydrochlorophyll and the hydroxyl radical. The former then again transfers its hydrogen to the magnesium-carbonic acid complex and the resulting dehydrochlorophyll again absorbs light. After the transfer of four hydrogen atoms to the magnesium complex with carbonic acid, the dehydro- and monodehydro-compounds are reconverted into chlorophyll by the light reaction and by a reaction in which water and monodehydrochlorophyll form the hydroxyl radical and chlorophyll.

Franck¹¹⁴ believed that the Willstätter mechanism, with monodehydrochlorophyll as the significant compound, could be altered slightly to correspond to the energy yields of the reaction and with the data of the Kautsky fluorescence curves. The initial rise in the Kautsky curve corresponds to a photo-process in which hydrogenated chlorophyll gives monodehydrochlorophyll and atomic hydrogen, the latter reacting with oxygen and water to give hydrogen dioxide. The photochemical yield of this reaction is poor. The subsequent drop in the fluorescence corresponds to a process in which monodehydrochlorophyll reacts with carbon dioxide with the production of hydroxychlorophyll and formic acid. In subsequent reactions in light, monodehydrochlorophyll, formaldehyde and hydrogen peroxide are produced. During the slow dark reaction, the original hydrogenated chlorophyll is reformed. It will be noted that the Franck theory assumes a photo-dissociation of a lightly bound hydrogen atom from chlorophyll. The recombination of this hydrogen atom produces a chemiluminescence of the same color as that of the fluorescence. It is, therefore, possible to determine from the fluorescence wave-length limits the energy required for the separation of the hydrogen atom. From the long wave-length limit of the narrow fluorescent band at 6800A, this is concluded to be 41.4 kcal.

The reactions of the Franck preparatory photoprocesses are written:

- (1) $\text{HH-Chlorophyll} + h\nu \longrightarrow \text{H-Chlorophyll} + \text{H}$.
- (2) $\text{H} + \text{O}_2 \longrightarrow \text{O}_2\text{H}$
- (3) $\text{O}_2\text{H} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{O}_2 + \text{OH}$
- (4) $\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O}_2$.

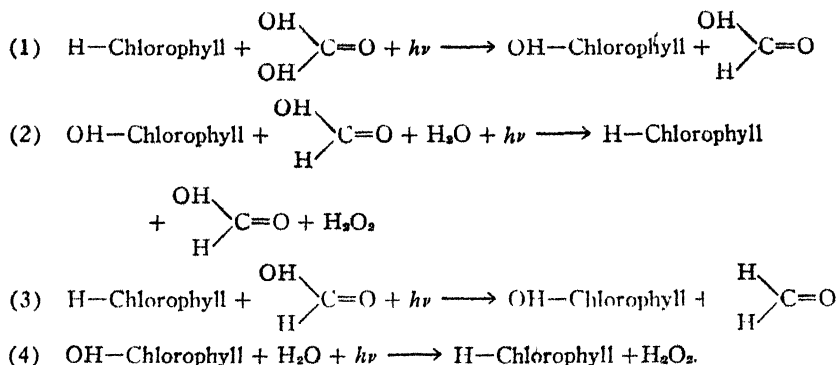
¹¹¹ Conant, J. B., Dietz, E. M., and Kamerling, S. E., *Science*, **73**, 268 (1931)

¹¹² Stoll, A., *Naturwiss.*, **20**, 955 (1932).

¹¹³ Willstätter, R., *Naturwiss.*, **21**, 252 (1933).

¹¹⁴ Franck, J., *Naturwiss.*, **23**, 226 (1935); *Chem. Rev.*, **17**, 443 (1935).

The equations for the assimilation process proper are written:



These equations were held to be energetically possible. In (1) and (3), light causes a change in position of an hydroxyl group of the bound carbonic or formic acid with a hydrogen atom of chlorophyll. In each case the hydrogen atom is the more firmly bound.

As to the possibility of reactions (2) and (4) it is said that it is necessary to supply enough energy to dissociate water into H and OH and in addition to separate the OH from the chlorophyll residue. The former requires 115 kcal. and the latter about 20 kcal., assuming the hydroxyl group to be at most half as firmly bound as the hydrogen on chlorophyll. There are available 41 kcal. by absorption of a quantum, and the same amount by the binding of a hydrogen atom on the chlorophyll residue and finally 52 kcal. from the combination of two hydroxyl groups to hydrogen peroxide. The new feature in the Franck formulation is the production of the more loosely bound OH-chlorophyll; this was believed to overcome the energetic difficulties in the previous formulation of the mechanism by Willstätter.

Oxygen is assumed necessary only for the preparatory processes. In its absence, irradiation would lead to the production of some carbon dioxide and the strongly fluorescent dehydrochlorophyll. This was believed to lose its energy by fluorescence most readily. This was held to explain the Kautsky curves in the absence of oxygen in which the fluorescence rose rapidly to a maximum after which it remained constant. Kautsky,¹¹⁵ however, states that his curve of this type was obtained in the presence of small amounts of oxygen, but not in its absence. When oxygen was absent, he could observe no fluorescence. Moreover, Kautsky maintains that his conception of the processes is in agreement with the work of Warburg on the separation of the process into a photochemical one and the Blackman reaction.

The study of fluorescence spectra has been extended to that of pheophorbide-*b* by Knorr and Albers,¹¹⁶ who follow its change during irradiation in the presence of various gases, oxygen, nitrogen and carbon dioxide.

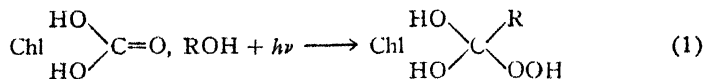
Wohl¹¹⁷ shows that the energy of four quanta of 6800Å, light which still gives photosynthesis, is smaller than the energy difference between the initial and final

¹¹⁵ Kautsky, H., *Naturwiss.*, **23**, 389 (1935); Kautsky, H., and Flesch, W., *Biochem. Z.*, **284**, 412 (1936); Kautsky, H., and Marx, A., *Naturwiss.*, **24**, 317 (1936); *Biochem. Z.*, **290**, 248 (1937); Kautsky, H., and Hormuth, R., *Naturwiss.*, **24**, 650 (1936); *Biochem. Z.*, **291**, 285 (1937); Kautsky, H., *Ibid.*, **291**, 271 (1937).

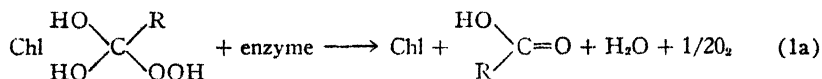
¹¹⁶ Knorr, H. V., and Albers, V. M., *Phys. Rev.*, **47**, 329 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 87, 98 (1935).

¹¹⁷ Wohl, K., *Z. physik. Chem.*, **31B**, 152 (1935); see also Gaffron, H., and Wohl, K., *Naturwiss.*, **24**, 81, 103 (1936).

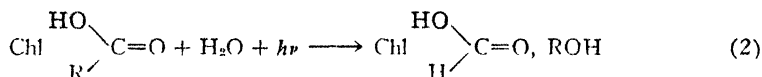
products of the overall reaction for the Franck mechanism, 192 kcal. At 6600Å four quanta give 172 kcal. Franck and Herzfeld¹¹⁸ suggest that for such a fluorescent, polyatomic molecule as chlorophyll, which has many degrees of freedom, the missing 20 kcal. may be supplied from the thermal energy. Franck has subsequently altered his suggested mechanism.¹¹⁹ The preparatory reaction was shown unnecessary by Gaffron.¹²⁰ The assumption of hydrogen peroxide is avoided in Franck's most recent mechanism. The chlorophyll-carbonic acid complex is assumed to be attached to an organic molecule ROH. The absorption of a quantum is thought to convert this into a peracid.



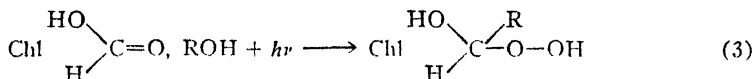
In a thermal enzyme reaction, this peracid is converted into an acid with liberation of oxygen.



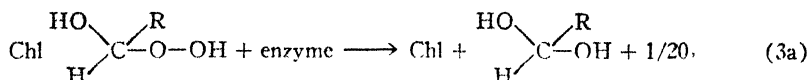
Absorption of another quantum produces formic acid.



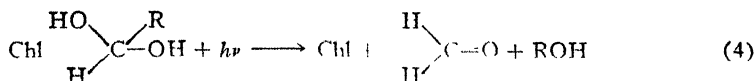
This in turn on absorption of a quantum produces a peraldehyde



which may then liberate oxygen in a thermal enzyme process.



The aldehyde on absorption of a quantum may then produce formaldehyde.



It is not possible in a limited space to discuss the mathematical developments of these reactions made by Franck, and their application to the rapidly accumulating body of experimental data. Gaffron suggests that a free-moving enzyme of the Blackman reaction forms in the dark an inactive dissociable oxygen compound. The complex can be activated by excess light energy when in a reducing location. He believes this may explain the observed rapid oxygen consumption directly after intensive illumination, and the high temperature coefficient of the induction.¹²¹

Wohl gives reasons for believing the Franck and Herzfeld reaction chain

¹¹⁸ Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, **41**, 97 (1937); Franck, J., *J. Wash. Acad. Sci.*, **27**, 317 (1937).

¹¹⁹ Franck, J., and Herzfeld, K. F., *J. Chem. Physics*, **5**, 237 (1937).

¹²⁰ Gaffron, H., *Naturwiss.*, **23**, 528 (1935).

¹²¹ Gaffron, H., *Naturwiss.*, **25**, 460 (1937); *Chem. Abs.*, **31**, 8557 (1937); *Naturwiss.*, **25**, 715 (1937); *Chem. Abs.*, **32**, 2977 (1931).

mechanism kinetically impossible.¹²² It is recently suggested by Baas-Becking and Hanson¹²³ that in the chloroplast the chlorophyll molecules occur in planes and are oriented in tetrads with the pentanon ring of each pointing to the same center, and that orthocarbonic acid is fixed at this center by the active hydrogen atoms of the four chlorophyll molecules.

Knoll, Matthews and Crist regard the Blackman reaction as an enzymatic decomposition of a peroxide formed in the photo-process. They find it the rate-determining process in the oxygen evolution at high light intensities and high carbon dioxide concentrations.¹²⁴

Because of their highly controversial and speculative nature, further consideration of the details of theories of the photosynthetic mechanism must be left to the specialist in this most important field.

Photosynthetic Units. In intermittent light experiments on cells with varied chlorophyll content, Emerson and Arnold¹²⁵ showed that for every 2480 molecules of chlorophyll one molecule of carbon dioxide was reduced in a single flash. This means either that the quantum efficiency is very low or that most of the light is absorbed by chlorophyll molecules not in contact with carbon dioxide. The suggestion was made that 2480 molecules function as a unit to reduce one molecule of carbon dioxide. The mean time for a unit to complete the cycle of photochemical and Blackman reactions was calculated to be between 0.01 and 0.02 second. The existence of such a photosynthetic unit was subsequently detected in work on six plant species.¹²⁶ More recently, Kohn¹²⁷ by measuring the oxygen production on exposure of green algae to flashes from a neon tube found only 360 molecules of chlorophyll to comprise the photosynthetic unit. Weiss¹²⁸ accounts for the existence of the unit by assuming that about 500 molecules in the interior of a lipid phase absorb and hand on the necessary quanta for one molecule on the surface. He also believes ferrous ions at the surface play a role in the reduction. It may be noted that Franck regards the assumption of photosynthetic units as unnecessary. Weiss also discusses the mode of transfer of excitation energy from molecule to molecule in the complex.¹²⁹

Important studies have recently been made on the course of photosynthesis in certain purple bacteria which promise to throw some light on the evolution of photosynthetic mechanisms. Van Niel¹³⁰ observed that some of these organisms require the absorption of but one quantum. On the other hand, French¹³¹ states that the process is similar to that in green plants. Recently, the quantum yield has been found to be much lower, twelve to eighteen quanta (8500-8900 or 5900A) being required to reduce a molecule of carbon dioxide.¹³²

The possibility that a chromoprotein as phycoerythrin may act as the sensitizer in the red algae has been discussed by Wurmser¹³³ and by Moore, Whitley and

¹²² Wohl, K., *Z. physik. Chem.*, **B37**, 122, 169 (1937).

¹²³ Baas-Becking, L. G. M., and Hanson, E. A., *Proc. Acad. Sci. Amsterdam*, **40**, 792 (1937); *Chem. Abs.*, **32**, 2178 (1938).

¹²⁴ Knoll, A. F., Matthews, F. L., Jr., and Crist, R. H., *J. Chem. Phys.*, **6**, 109 (1938). For recent kinetic data on photosynthesis, especially the induction period, in single fronds of *Cabomba caroliniana*, see E. L. Smith, *J. Gen. Physiol.*, **20**, 807 (1937); **21**, 151 (1937).

¹²⁵ Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **16**, 191 (1932).

¹²⁶ Arnold, W., and Kohn, H. I., *J. Gen. Physiol.*, **18**, 109 (1934); see also Arnold, W., *Ibid.*, **17**, 135 (1933).

¹²⁷ Kohn, H. I., *Nature*, **137**, 706 (1936).

¹²⁸ Weiss, J., *J. Gen. Physiol.*, **20**, 501 (1937). See also Wohl, K., *Z. physik. Chem.*, **B37**, 105, 186, 209 (1937).

¹²⁹ Weiss, J., *Nature*, **141**, 248 (1938).

¹³⁰ Van Niel, C. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 138 (1935); *Chem. Abs.*, **30**, 6782 (1936); Gaffron, H., *Biochem. Z.*, **275**, 301 (1935); van Niel, C. B., *Bull. assoc. diplomes microbiol. faculte pharm. Nancy*, No. 13, 3 (1936); Sapozhnikov, D. I., *Biokhimiya*, **2**, 181 (1937); *Chem. Abs.*, **31**, 7923 (1937).

¹³¹ French, C. S., *Science*, **84**, 575 (1936); *J. Gen. Physiol.*, **21**, 71 (1937). See also Nakamura, H., *Acta Phytotom. (Japan)*, **9**, 189, 231 (1937); *Chem. Abs.*, **31**, 7465 (1937); *Acta Phytotom. (Japan)*, **10**, 211 (1937); *Chem. Abs.*, **32**, 210 (1938).

¹³² Eymers, J. G., and Wassink, E. C., *Enzymologia*, **2**, 291 (1938); *Chem. Abs.*, **32**, 5436 (1938).

Webster.¹³⁴ Montfort¹³⁵ finds fucoxanthin in brown algae to have a definite physiological function in increasing the photosynthetic efficiency in blue light. Instead of falling off from the red to the blue, it increases in some species to a value three times as high as required by the quantum theory and to more than twice the efficiency in red light. Carotene and xanthophyll in plants in which they are present appear not to have a part in increasing the efficiency.¹³⁶ In *Chlorella*, respiration and photosynthesis are retarded by 88 per cent heavy water.¹³⁷ Pratt, Craig and Trelease¹³⁸ found that although 99.9 per cent heavy water depressed photosynthesis to 41 per cent of that in water in bright light, it showed little difference from water at low light intensities. The lower rate suggested that deuterium exchanges for hydrogen at a critical point in some molecule involved in one of the dark reactions. The respiration is less retarded by heavy water. The temperature coefficients of photosynthesis in H₂O and D₂O were the same in the range 10-30 °C, but higher for D₂O than water between 30 and 46 °C.

Plane-polarized light formed no different amount of starch from that produced by ordinary light in the leaves of *Allium cepa* or *Helianthus annuus*.¹³⁹ On the other hand, elliptically polarized light retarded the formation of carbohydrates in leaves.¹⁴⁰ Leaves were also said to absorb a larger amount of energy from polarized than from ordinary light.

It has been suggested that ester formation in plants is due to the ultraviolet rays of sunlight.¹⁴¹ Pal¹⁴² finds light necessary for not only the conjugation of *Spirogyra*, but also for the conversion of carbohydrates to fats or oils. In darkness, there occurs a conversion of fats to carbohydrates. Our knowledge of the photosynthesis of volatile oils and allied principles is still speculative.¹⁴³

Photosynthesis of Proteins. Baly, Heilbron and Hudson¹⁴⁴ reported that activated formaldehyde, produced photochemically according to the disputed methods of Baly, reacts rapidly with nitrites with the formation of hydroxamic acid, the reaction taking precedence over the polymerization of the formaldehyde to reducing sugars.¹⁴⁵ Formhydroxamic acid is assumed by Baly to react further in various ways with activated formaldehyde to give rise to α -amino acids and nitrogen bases, including even alkaloids. Baly and co-workers believed they had isolated two alkaloids and an amino-acid like histidine formed in this manner in *in vitro*

¹³³ Wurmser, R., *Trav. Inst. Physiol. Gen. Strassbourg*, 1919-20, *Chem. Abs.*, **19**, 3289 (1925).

¹³⁴ Moore, B., Whitley, E., and Webster, T. A., *36th Ann. Report. Oceanography*, (Liverpool) 1922; *Chem. Abs.*, **19**, 3289 (1925).

¹³⁵ Montfort, C., *Jahrb. wiss. Botan.*, **83**, 725 (1936); *Chem. Abs.*, **31**, 4693 (1937); Schmidt, G., *Jahrb. wiss. Botan.*, **85**, 554 (1937); *Chem. Abs.*, **32**, 3788 (1938).

¹³⁶ See, however, Sapozhnikov, D. I., *Biokhimiya*, **2**, 730 (1937); *Chem. Abs.*, **32**, 6673 (1938).

¹³⁷ Shibata, K., and Watanabe, A., *Acta Phytochim.*, **9**, 107 (1936); *Chem. Abs.*, **30**, 8272 (1936).

¹³⁸ Pratt, R., Craig, F. N., and Trelease, S. F., *Science*, **85**, 271 (1937); *Am. J. Botan.*, **24**, 232 (1937); Curry, J., and Trelease, S. F., *Science*, **82**, 18 (1935); Pratt, R., and Trelease, S. F., *Am. J. Botany*, **25**, 133 (1938).

¹³⁹ Dastur, R. H., and Asana, R. D., *Ann. Botany*, **46**, 879 (1932); *Chem. Abs.*, **27**, 2709 (1933); Johnston, E. S., *Smithsonian Inst. Pub. Misc. Collections*, **96**, No. 3 (1937).

¹⁴⁰ Dastur, R. H., and Gunjkar, L. K., *Ann. Botany*, **48**, 1003 (1934); **49**, 273 (1935); *Chem. Abs.*, **29**, 1456, 5877 (1935). See, however, Semmens, E., *Nature*, **134**, 813 (1934); **130**, 243 (1932); *Bot. Gaz.*, **90**, 412 (1930); *Chem. Abs.*, **25**, 983 (1931).

¹⁴¹ Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1804 (1914).

¹⁴² Pal, N. L., *New Phytol.*, **33**, 242 (1934); *Chem. Abs.*, **29**, 2997 (1935).

¹⁴³ Singleton, F., *Chem. & Ind.*, **50**, 989 (1931).

¹⁴⁴ Baly, E. C. C., Heilbron, I. M., and Hudson, D. P., *J. Chem. Soc.*, **121**, 1078 (1922); *J. Soc. Chem. Ind.*, **41**, 609A (1922); *Chem. Abs.*, **16**, 3463 (1922); Baly, E. C. C., Heilbron, I. M., and Stern, H. J., *J. Chem. Soc.*, **123**, 185 (1923); *Chem. Abs.*, **17**, 1421 (1923).

¹⁴⁵ Either diffused daylight or ultraviolet, according to Baudisch, O., [*Ber.*, **44**, 1009 (1911); **49**, 1176 (1916); **51**, 793 (1918)] causes methanol to react with potassium nitrite, yielding the potassium salt of formhydroxamic acid, $\text{CHOH}=\text{NOK}$.

experiments. Snow and Stone,¹⁴⁶ however, pointed out that the identification of these alkaloids had been insufficient, and that certain simpler compounds would yield the tests which had been described.

Burk¹⁴⁷ made over five hundred experiments to detect the formation of complex nitrogen compounds by the action of intense sunlight and colored inorganic catalysts upon ammonia and such carbon compounds as carbon dioxide, formic acid, formaldehyde or dextrose. The results were in general negative. The only type of reaction observed was the oxidation of ammonia to nitrate which occurred in the presence of ferric chloride, or to nitrites and nitrates in the presence of zinc or mercuric oxide. Hydroxylamine and hydrogen peroxide, or complex nitrate compounds were never produced.

Recently, however, Bhargava and Dhar,¹⁴⁸ claimed success in the production of nicotine and methylamine by exposing a small quantity of ammonia and a 2 per cent solution of formaldehyde to a mercury-vapor lamp or to sunlight in the presence of zinc oxide, titanium dioxide or copper carbonate. Dhar and Mukherjee¹⁴⁹ also claimed that a similar exposure of 0.5N solutions of ammonium, potassium or sodium nitrate, containing glucose, tartaric acid, glycerol, arabinose, fructose, mannose or galactose, gave positive colorimetric tests for amino-acids. The yields were best with ammonium nitrate and none were formed in darkness or when ammonium hydroxide was used as the nitrogen source. The amounts of amino-acids reached a maximum in four to six hours, after which they were removed by oxidation.

Urban¹⁵⁰ finds that ammonia nitrogen is taken up by *Chlorella* and other forms more rapidly in light. Loose and Pearsall¹⁵¹ find that in this organism the velocity of protein synthesis is five times as great in light as in darkness. If sufficient carbohydrate is available, the final equilibrium is similar.¹⁵²

According to Tottingham and Louwsma,¹⁵³ a 50 to 400 per cent increase in the blue, violet and long ultraviolet rays increases the absorption of nitrates and to a smaller extent the synthesis of proteins by wheat. When the short wave-length limit is extended from 4000 to 3700A, there is no change. When it is extended to 3000A there is an increase in the absorption but not in the assimilation of nitrates. The admission of rays as short as 2800A decreases the formation of tissue and proteins. Although increasing the proportion of blue to violet light by supplementing Mazda lamps by carbon arcs increases the percentage of protein in young wheat plants, it decreases the pentosans and crude fiber.¹⁵⁴ Solar ultraviolet causes more marked changes and increases the percentage of lipids and of uronic acid.

In tobacco stalks and leaves, light probably leads to a synthesis of glutamine.

¹⁴⁶ Snow, O. W., and Stone, J. F. S., *J. Chem. Soc.*, 123, 1509 (1923); *Chem. Abs.*, 17, 2865 (1923).

¹⁴⁷ Burk, D., *J. Phys. Chem.*, 31, 1338 (1927). See also Calcagni, G., *Rev. biol.*, 22, 92 (1937); *Chem. Abs.*, 32, 4625 (1938).

¹⁴⁸ Bhargava, L. N., and Dhar, N. R., *J. Indian Chem. Soc.*, 10, 453 (1933); *Chem. Abs.*, 28, 413 (1934).

¹⁴⁹ Dhar, N. R., and Mukherjee, S. K., *Nature*, 134, 499 (1934); *J. Indian Chem. Soc.*, 11, 727 (1934); *Chem. Abs.*, 29, 2450 (1935).

¹⁵⁰ Urban, O., *Jahrbuch Wiss. Botan.*, 75, 1 (1932); *Chem. Abs.*, 26, 4629 (1932).

¹⁵¹ Loose, L., and Pearsall, W. H., *Nature*, 171, 362 (1933).

¹⁵² For the blue-green alga, *Nostoc*, see Allison, F. E., and Hoover, S. R., *Trans. 3rd Intern. Congress Soil Sci. Oxford*, 1, 145 (1935); *Chem. Abs.*, 29, 8203 (1935).

¹⁵³ Tottingham, W. E., and Louwsma, H. W., *J. Am. Chem. Soc.*, 50, 2436 (1928); Tottingham, W. E., Stephens, H. L., and Lease, E. J., *Plant Physiol.*, 9, 127 (1934); *Chem. Abs.*, 28, 3444 (1934).

¹⁵⁴ Tottingham, W. E., and Lease, E. J., *Science*, 80, 615 (1934); *J. Am. Chem. Soc.*, 57, 2613 (1935).

Malic acid diminishes and citric acid increases in cultures in darkness. Oxalic acid is unchanged.¹⁵⁵

Small amounts of ultraviolet light cause an increase in the nitrogen content of *Sinapis alba*.¹⁵⁶

¹⁵⁵ Vickery, H. B., Pucher, G. W., Wakeman, A. J., and Leavenworth, C. S., *Conn. Agr. Expt. Sta., Bull.* 407, 111 (1938); *Chem. Abs.*, 32, 5441 (1938); *J. Biol. Chem.*, 119, 369, 523 (1937).

¹⁵⁶ Kabos, W. J., *Rec. trav. botan. neerland.*, 33, 447 (1936), *Chem. Abs.*, 32, 212 (1938).

Chapter 44

Effects of Ultraviolet Radiations on Plants

Although de Lima² found that ultraviolet light has no effect on germinating rye, others have claimed that, at least in certain wave-length regions, it stimulates germination. DeWolf and Fry³ proposed to subject seeds before sowing to the action of ultraviolet rays from a mercury-vapor lamp or other source, with or without previous treatment in water or a solution of sodium nitrate or manure. Heinisch⁴ believed the germinating power of unripe barley to be considerably improved by ultraviolet irradiation. If, however, the same barley had been allowed to ripen before harvesting, the effect of irradiation was less striking.

Many workers have, however, shown that in general unfiltered mercury arc irradiations are harmful to germinating plants. In the case of dry seeds, lack of penetration of the coats may prevent these effects from becoming readily apparent. There is general agreement that if radiations of wave-length shorter than 2900A are applied, lethal action will result, as discussed in Chapter 33 in the case of bacteria and other organisms.⁵

Some authors have recently claimed that there is a stimulating action of ultraviolet rays longer than the lethal limit. Higgins and Sheard⁶ found wave-lengths between 3200 and 3900A transmitted by a Corning ultraglass filter 586 AW, particularly effective in producing germination and growth of cucumber seeds. Rays between 2700 and 3200A delayed the time of germination and reduced the rate of growth.

Gilles⁷ believed the germination of lentil and turnip seeds accelerated but their growth somewhat diminished by mercury-arc irradiation. A few other workers claimed to have obtained a stimulating action by filtered ultraviolet, applying wave-lengths in the region of 3650A or those of daylight.⁸

These reports have been criticized by Popp and Brown,⁹ largely because the

¹ The interested reader may find summaries of the extensive work on the effects of visible light in the book edited by Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Company, Inc., 1936.

² de Lima, P., *Compt. rend.*, **105**, 493 (1930).

³ De Wolf, C. E., and Fry, H. E., *British F.* **23**, 339, Oct. 15, 1913; *Chem. Abs.*, **9**, 950 (1915).

⁴ Heinisch, O., *Wochschr. Brau.*, **49**, 348 (1932); *Chem. Abs.*, **27**, 3028 (1933); de Fazi, R., *Atti Acad. Lincei*, **11**, 1022 (1930); *Chem. Abs.*, **25**, 3121 (1931); Kamenskii, K. V., and Orekhova, T. A., *Bull. Applied Botany, Genetics Plant Breeding (U.S.S.R.)*, *Ser.* **IV**, No. 2, 67 (1937); *Chem. Abs.*, **31**, 5843 (1937).

⁵ Carl, *Beitr. Biol. Pflanz. (Cohn's)*, **12**, 435 (1914); Sibilia, C., *Bull. soc. Bot. Ital.*, 160 (1925) cited by Popp, H. W., and Brown, F., in Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936, II, Chapter 26. Dane, H. R., *Science*, **66**, 80 (1927); Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, **5**, 138 (1927); Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **101**, 820 (1929).

⁶ Higgins, G. M., and Sheard, C., *Plant Physiol.*, **2**, 325 (1927); *Chem. Abs.*, **22**, 3685 (1928).

⁷ Gilles, E., *Compt. rend. soc. biol.*, **109**, 739 (1932); *Chem. Abs.*, **27**, 3969 (1933). Gilles reviews work subsequent to 1881 and concludes light less than 2900A favors germination, but affects adult plants adversely. The range 2900 to 3100A favors plant development. *Ann. univ. Lyon, Ser. 3*, **1C**, 38 (1936); *Chem. Abs.*, **32**, 7965 (1938).

⁸ Valentin, H., *Pharm. Ztg.*, **75**, 982, 995, 1005 (1930); *Chem. Abs.*, **25**, 120 (1931); Jacobi, *Beitr. Biol. Pflanz. (Cohn's)*, **16**, 405 (1928); Masure, M. F., *Botan. Gaz.*, **93**, 21 (1928); *Chem. Abs.*, **26**, 2487 (1932).

⁹ Popp, H. W., and Brown, F., *Bull. Torrey Botan. Club*, **60**, 161 (1933); *Chem. Abs.*, **27**, 2709 (1933); "Biological Effects of Radiation," edited by Duggar, B. M., **II**, 851, New York, McGraw-Hill Book Company, Inc., 1936.

possible effects of infrared rays upon the irradiated plants were not adequately eliminated. Very extensive studies by Popp led to the following generalizations:¹⁰

1. Exposure of dry seeds to the full ultraviolet of a quartz mercury-vapor arc have little or no effect on later germination and growth, even after 188 hours' exposure. This may be due to inability of the short rays to penetrate the dry seed coat.

2. Exposures of less than two hours' duration on soaked seeds that have not yet begun to sprout did not have a marked effect on germination. Probably here too there is not enough penetration of the short rays in so short a time to cause any permanent injury.

3. Longer exposures to the open arc decrease the rate and the amount of germination, inhibit growth and development and finally cause death of the plant. The wavelengths below 3000A are more effective in this respect than are those above.

4. In general, cotyledons of seeds exposed to ultraviolet seems to have difficulty in emerging from the seed coat, but if they do get through they are not seriously injured by the short rays until after long exposures, 120 hours.

5. Chlorophyll appears in the cotyledons of seedlings raised under the open arc about as rapidly as it does in ordinary light, but never reaches the intensity it does in daylight.

6. Ultraviolet light does not seem to be necessary for a development of the reddish-purple pigment on the under side of the cotyledons of mustard. Under Noviol glass which screens off all ultraviolet and in the dark, this pigment always appears. It reached its deepest intensity uniformly in the greenhouse plant where comparatively little ultraviolet was present.

7. Geranium plants exposed to the open arc for 6 hours, after being in the dark for 24 hours showed no difference in appearance at the end of the 6 hours, but tests of the leaves for starch at this time were entirely negative. But in ordinary light, starch can be located in these leaves after an hour or less.

8. In no case were new leaves formed in mustard under ultraviolet rays. The new leaves were formed in sunflower, Canada field peas, oats and corn, but these leaves were all killed in a day or two after they were formed.

9. A few plants were able to grow under the open arc in all of the series but in no case was there any further development than would result from the food stored in the seeds.

10. Seedlings that do not survive will live longer under its rays than those grown in the dark at the same time. Since there is apparently very little food synthesis, this may be due to a retarding of enzyme action or other germination processes. If these seedlings after being exposed from 6 to 8 hours a day for 10 to 15 days are removed to the greenhouse, they immediately start to develop normally; but exposed seeds that have not germinated under ultraviolet rays cannot be made to germinate in this way later.

11. Seedlings grown in daylight in the absence of ultraviolet or in complete darkness and then exposed to the open arc were killed after 6 to 20 hours' exposure. Similarly, the leaves of mature plants of geranium or coleus with 6 hours' exposure to the open arc will have a burnt appearance the next day and fall off. In the seedlings, the young leaves and next the stems are most susceptible to injury. Apparently, those grown under the arc from the start are able to adapt themselves to it to a certain extent. Finally, of course, they too are killed.

12. When all ultraviolet was screened off, mustard seeds in visible light gave as high a rate and amount of germination as they did in complete darkness. This same effect was produced, however, when the seeds were exposed to all the rays between 6000 and 3000A. If the ultraviolet between 3000 and 4000A was the only radiation falling on the seeds, a somewhat lower rate and amount of germination were observed. Apparently, the inimical effects of the regions between 4000 and 3000A are overcome when visible light is falling on the plants at the same time.

13. No striking differences in growth and development of seedlings of mustard were observed when all ultraviolet was screened off, as compared with seedlings grown under the rays from 6000 to 3000A. If, however, the region between 4000 and 3000A was the only one to which the seedlings were exposed, a distinct retarding of growth and development occurred.

14. Bacteria and general damping-off fungi do not develop in the rays of the open arc but will if the region below 3000A is screened off.

¹⁰ Private communication from Prof. H. W. Popp.

More Mature Plants. A large number of investigations have been devoted to the determination of the effects on growth which may be ascribed to the ultraviolet portion of the solar spectrum. Maquenne and Demotussy¹¹ early stated that ultraviolet rays properly applied are very beneficial to flowers and other vegetation. In various species, Tottingham and Moore¹² found seed production, root storage or earliness of blooming were favored by irradiation under Vitaglass as compared with common glass. Certain species which do not possess winter hardening capacities were more subject to frost injury following early development under this glass. In some instances an increase in the percentage of protein or non-protein, non-lipid nitrogen was found in the tissues produced under Vitaglass. The most consistent compositional response to this irradiation was believed to be an increased percentage of lipids in the dry matter, but this was not very definite. Similar results were also reported for tomato seedlings by Tottingham,¹³ using a General Electric sunlamp. Popp¹⁴ believes that, although ultraviolet rays are not indispensable, the blue-violet end of the visible spectrum is necessary for the normal, vigorous growth of the plant.

Subsequently, Popp and Brown¹⁵ reviewed a number of papers in which a stimulating effect of the ultraviolet longer than 2900A had been claimed. It is scarcely necessary to discuss these here. In practically all of them it was possible to find flaws in the methods employed. Arthur,¹⁶ at the Boyce Thompson Institute was unable to find that the use of ultraviolet-transmitting glasses offered any advantages in plant growth.

Singh, Kapoor and Choudhri¹⁷ found exposure of plants to ultraviolet rays for periods of five minutes or more at intervals of less than 14 days to be detrimental to growth.

Ultraviolet produces growth inhibition and morphological changes in *Aspergillus*, according to Kresling and Shtern.¹⁸

The growth substance, 3-indolepropionic acid, turns yellow under ultraviolet irradiation and acquires an unpleasant odor. At the same time the blue fluorescence of its acid solutions decreases, as does its ultraviolet absorption band. After several hours of irradiation, the solution loses its ability to retard the root growth of corn and bean roots in Knop's solution.¹⁹ Similarly, the growth substance in oat coleoptiles loses its activity when intensely irradiated with a mercury arc.²⁰

The formation of chlorophyll is favored by visible light of low intensities; high intensities of light tend to destroy it. Relatively few observations have been made on the influence of ultraviolet light upon its formation. According to Tottingham,²¹ tomato leaf tissue grown under glass and under Vitaglass showed respectively,

¹¹ Maquenne, L., and Demotussy, E., *Compt. rend.*, **149**, 756 (1909).

¹² Tottingham, W. E., and Moore, J. G., *J. Agr. Research*, **43**, 133 (1931); *Chem. Abs.*, **25**, 5913 (1931).

¹³ Tottingham, W. E., *Plant Physiol.*, **7**, 551 (1932).

¹⁴ Popp, H. W., *Am. J. Botan.*, **13**, 706 (1926); *Chem. Abs.*, **22**, 3191 (1928); *Botan. Gaz.*, **82**, 306 (1926); *Chem. Abs.*, **21**, 435 (1927). See also Arthur, J. M., and Harvill, E. K., *Contrib. Boyce Thompson Inst.*, **8**, 433 (1937); *Chem. Abs.*, **31**, 6285 (1937).

¹⁵ Popp, H. W., and Brown, F., "Biological Effects of Radiation," edited by Duggar, B. M., II, 853, New York, McGraw-Hill Book Company, Inc., 1936.

¹⁶ Arthur, J. M., *Sci. Monthly*, **31**, 343 (1930); Arthur, J. M., and Newell, J. M., *Am. J. Botan.*, **16**, 338 (1929).

¹⁷ Singh, B. N., Kapoor, G. P., and Choudhri, R. S., *Botan. Gaz.*, **97**, 649 (1936); *Chem. Abs.*, **30**, 4197 (1936).

¹⁸ Kresling, E. K., and Shtern, E. A., *Zentr. Bakt. Parasitenk.*, **II Abt.** **95**, 327 (1936); *Chem. Abs.*, **30**, 5256 (1936).

¹⁹ Hare, D., and Kersten, H., *Plant Physiol.*, **12**, 509 (1937).

²⁰ Burkholder, P. R., and Johnston, E. S., *Smithsonian Misc. Coll.*, **95**, No. 20 (1937).

²¹ Tottingham, W. E., *Science*, **75**, 223 (1932); *Chem. Abs.*, **26**, 2488 (1932).

chlorophyll 1.76 and 1.50 per cent, carotene, 0.007 and 0.017 per cent, and xanthophyll 0.053 and 0.368 per cent. From the lipid fraction, there were obtained sterols to the extent of 0.81 and 0.87 per cent. The conclusion was that the formation of carotenoids and sterols is favored by irradiation under Vitaglass, but the chlorophyll declines. The ratio of chlorophyll-*a* to chlorophyll-*b* is lowered by irradiating leaves with monochromatic light largely absorbed by chlorophyll-*a*.²²

Colla²³ ascribes the formation of chlorophyll in wheat, beans and lentils to the action of radiations in the range 3300 to 3900A, without the aid of visible rays.

Stoklasa²⁴ early observed that after irradiation by wave-lengths 3000 to 5000A (mercury arc), the young leaves of the etiolated seedlings of *Pisum*, *Zea mais*, *Avena* and *Hordeum* showed a dark green coloration in two hours. With solar irradiation a similar color was formed only after six hours of exposure. He also believed that chlorophyll exerts a protective action against ultraviolet rays of daylight. The cells of flowers as well as those of plants grown under glass were more sensitive toward ultraviolet rays than the cells of green leaves. Jirovec²⁵ finds the chlorophyll-free stems of *Euglena gracilis* considerably more sensitive to ultraviolet rays than are green stems of the same species. Dangeard²⁶ found the energy of wave-lengths shorter than 4900A from a Nernst lamp incapable of aiding the formation of chlorophyll, but Sayre²⁷ has found that if the intensity is high enough chlorophyll may be developed by the wave-length region 3000 to 4000A. The function of the ultraviolet is still, however, uncertain.²⁸

A colorless protochlorophyll may be present in sunflower seedlings grown in the dark, but etiolated plants must be irradiated before chlorophyll can form in them.²⁹ Beck finds that xanthophyll and carotene are formed in the dark. However, light may stimulate the production of these pigments.³⁰

Certain acid-fast bacteria produce pigment in darkness only after brief preceding exposures to ultraviolet light or longer exposures to incandescent lamp light.³¹

Wave-lengths in the region 2900 to 3100A were believed by Benedict³² to increase the dry weights of a number of plants, but not of corn. They also cause an increase in the calcium content, but the results with phosphorus were inconclusive. Wynd and Fuller³³ observed that when tomato and cucumber plants were irradiated daily through Vitaglass at 100 inches from an arc, after five weeks there was an increase in the calcium content as compared with that in controls. The phosphorus content decreased. Experiments of this type were conducted

²² Tottingham, W. E., and Dutton, H. J., *Science*, **87**, 214 (1938).

²³ Colla, S., *Boll. soc. ital. biol. sper.*, **4**, 298 (1929); *Chem. Abs.*, **23**, 4496 (1929).

²⁴ Stoklasa, J., *Strahlentherapie*, **6**, 119 (1915); *Zentr. Biochem. Biophys.*, **18**, 370 (1915).

²⁵ Jirovec, O., *Protoplasma*, **21**, 577 (1934); *Chem. Abs.*, **28**, 6765 (1934).

²⁶ Dangeard, P. A., *Botaniste*, **12**, xxii (1912). Cited in Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936.

²⁷ Sayre, J. D., *Plant Physiol.*, **3**, 71 (1928).

²⁸ See also Shirley, H. L., *Am. J. Botany*, **16**, 354 (1929).

²⁹ Beck, W. A., *Studies Inst. Divi Thomae*, **1**, 109 (1937); *Protoplasma*, **28**, 273 (1937); *Plant Physiol.*, **12**, 885 (1937); Voegelé, A. C., *Ibid.*, **12**, 929 (1937).

³⁰ Beck, W. A., *Studies Inst. Divi Thomae*, **1**, 217 (1937); Beck, W. A., Redman, R., and Schroeter, M. P., *Ibid.*, **1**, 245 (1937). See also Seybold, A., and Egle, K., *Planta*, **28**, 87 (1938); *Chem. Abs.*, **32**, 5443 (1938); Strain, H. H., *Plant Physiol.*, **13**, 413 (1938); *Chem. Abs.*, **32**, 8476 (1938); Stroti, A., *Jahrb. wiss. Botan.*, **86**, 1 (1938); *Chem. Abs.*, **32**, 8482 (1938).

³¹ Baker, J. A., *J. Bact.*, **35**, 625 (1938).

³² Benedict, H. M., *Botan. Gaz.*, **96**, 330 (1934); *Chem. Abs.*, **29**, 1131 (1935).

³³ Wynd, F. L., and Fuller, H. J., *Ann. Mo. Bot. Gardens*, **18**, 565 (1931); *Chem. Abs.*, **26**, 2215 (1932).

to determine whether sterols in the plant could be converted into a vitamin which aids the absorption of calcium by the plant as in the case of vitamin D in animals. According to Stewart and Arthur,³⁴ tomato, tobacco, datura, lettuce, and salvia, grown in periods of low light intensity and then irradiated by a quartz mercury arc, showed an increase in ash, and in calcium or phosphorus or both. If, however, the plants were grown in light of high intensity, they failed to exhibit these changes on irradiation. Cabbage did not show these changes. It responded at first by an increase in ash in the leaves and a decrease in the stem. Repeated irradiations caused an increase of ash of stem and leaves and an increase in calcium or phosphorus or both. The manganese and magnesium contents of plants were not affected by ultraviolet irradiation. Similar ash changes could be obtained by treating the plants with irradiated ergosterol.

Tomato plants previously grown on solutions lacking calcium or phosphorus showed no increase in ash, calcium or phosphorus on irradiation with a quartz mercury arc. The level of the supply of these elements and not their ratio determines the response to irradiation. In solutions low in phosphorus and high in calcium, irradiation increases the ash and calcium. In solutions low in calcium and high in phosphorus, the ash and phosphorus increased.³⁵

In experiments of Mitchell,³⁶ equal amounts of radiant energy from a 3000-watt carbon arc and a 2000-watt Mazda incandescent lamp were supplied for two weeks to tomato plants. Those under the arc grew less in height and synthesized more than twice as much solid matter and approximately four times as much acid-hydrolyzable materials and sugars as did those under the incandescent lamp. For equal incident energy, the arc was 53 per cent more efficient in electrical energy consumption in producing dry matter. But when the light from the two sources was balanced by a photronic cell, there was a more equal gain in dry weight and carbohydrates under both sources. Those plants under the arc then synthesized less solid matter per unit of time than did those under the incandescent lamp.

But little work has been done on the effect of ultraviolet on the respiration of plants. Masure³⁷ claimed that the region near 3650A, obtained by the use of a Corning G586AW filter, temporarily accelerates the respiration of pea seedlings. His work has, however, been criticized by Popp and Brown³⁸ on the ground that the filter used transmitted also infrared radiations and that these, rather than the ultraviolet, may have been the cause of the effects observed. Wynd, Fuller and Reynolds³⁹ believe that injurious raying of tomato plants stimulates respiration and peroxidase and, in general, catalase, but inhibits oxygenase. Non-injurious raying stimulated catalase. Comparatively weak irradiation of bean plants stimulated peroxidase.

Percival⁴⁰ finds that exposure to light coming through window glass causes a darkening of the mycelium of the fungus, *Fomes pini*. Exposures to ultraviolet rays of sunlight in addition to the visible spectrum caused a further darkening

³⁴ Stewart, W. D., and Arthur, J. M., *Contrib. Boyce Thompson Inst.*, 6, 225 (1934); *Chem. Abs.*, 28, 5853 (1934).

³⁵ Stewart, W. D., and Arthur, J. M., *Contrib. Boyce Thompson Inst.*, 9, 105 (1937); *Chem. Abs.*, 32, 1756 (1938).

³⁶ Mitchell, J. W., *Botan. Gaz.*, 99, 412 (1937); *Chem. Abs.*, 32, 1759 (1938).

³⁷ Masure, M. P., *Botan. Gaz.*, 93, 21 (1932); *Chem. Abs.*, 26, 2487 (1932).

³⁸ Popp, H. W., and Brown, F., *Bull. Torrey Botan. Club*, 60, 161 (1933); *Chem. Abs.*, 27, 2709 (1933).

³⁹ Wynd, F. L., Fuller, H. J., and Reynolds, E. S., *Ann. Missouri Botan. Gardens*, 22, 837 (1935); *Chem. Abs.*, 30, 3466 (1936).

⁴⁰ Percival, W. C., *Bull. N. Y. State Coll. Forestry*, 6, 1B, 72 pp. (1933); *Chem. Abs.*, 29, 2573 (1935).

of the mycelium and a suppression of aerial hyphae. Stephens ⁴¹ finds ultraviolet irradiation of certain strains of the fungus *Glomerella* greatly stimulated conidial production. Certain strains which had never been known to produce perithecia did so after irradiation if either pepsin, raffinose or magnesium sulfate was added to the nutrient medium.⁴²

Some applications of ultraviolet light in the treatment of plant diseases have been noted by Pichler and Wöber,⁴³ but x-rays were more efficient.

Attempts are being made in the U.S.S.R. to induce the formation of rubber in plants by treating them with ultraviolet rays. Novikov and Herber ⁴⁴ soaked seeds of the Tau-sagyz rubber plant in distilled water for 18 hours at 25°C., dried and irradiated them with a quartz mercury arc under varying conditions. After irradiation, the seeds were allowed to germinate at 25°C. for two days, after which the catalase activity was determined. In all irradiated seeds the catalase activity increased abruptly. Ultraviolet irradiation of the leaves of Tau-sagyz and *Asclepias*, previously saturated with 3-per cent sucrose solutions, caused these plants to continue the formation of rubber in the dark in a 3-per cent sucrose solution. Non-irradiated leaves, either saturated or unsaturated with sugar, not only formed no new rubber in the dark but even lost that which they had contained. Irradiated leaves not saturated with sugar did not produce any rubber.

During growth, plants from irradiated seeds were said not to have been attacked by aphids; they also shed their leaves later and recovered their foliage earlier, indications of increased life tonus.

From microchemical observations, Kiselev, Osipov and Kuz'mina,⁴⁵ concluded that the formation of rubber and closely related resinous material is a photo-synthetic process.

Exposure of apples to ultraviolet light produced injury and discoloration of the anthocyanins, according to Pearce and Streeter.⁴⁶ Freytag⁴⁷ finds that ultraviolet rays may produce necrotic pigmentation (probably melanin) in leaves and fruit skins. Oxygen is necessary for this. With certain leaves a change in permeability seems to result.

No significant increase in the glucoside yield could be obtained by growing digitalis plants under glass transparent to ultraviolet rays, according to recent experiments of Leonard and Arthur⁴⁸ which thus failed to confirm the prior claims of McCrae that this could be done.⁴⁹

Potato tubers irradiated for twenty days with a Uviol mercury arc or by Mazda lamps showed an increased solanine content, accompanied by the appearance of anthocyanin in the sprouts. Irradiation with red-orange light did not induce a significant increase in solanine but caused an increase in chlorophyll. Ultraviolet rays of about 3000A were believed to be effective in solanine formation.⁵⁰

⁴¹ Stephens, F. L., *Philippine Agr.*, 19, 265 (1930); *Chem. Abs.*, 25, 1274 (1931).

⁴² For data on cells of the prothallium of *Osmundia claytoniana* or *Pteris longifolia*, see Charlton, F. B., *Am. J. Botany*, 25, 431 (1938).

⁴³ Pichler, F., and Wöber, A., *Centr. Bakt. Parasitenk.*, II, 57, 319 (1922); *Chem. Abs.*, 17, 1270 (1923).

⁴⁴ Novikov, V. A., and Herber, E. K., *Compt. rend. Acad. Sci. U.R.S.S.*, 131 (1933); *Chem. Abs.*, 28, 1740 (1934).

⁴⁵ Kiselev, N. N., Osipov, A. P., and Kuz'mina, K. A., *Bull. Acad. Sci. U.R.S.S., Classe sci. math. Nat.*, 9, 1367 (1935); *Chem. Abs.*, 29, 5481 (1935).

⁴⁶ Pearce, G. W., and Streeter, L. R., *J. Biol. Chem.*, 92, 743 (1931); see also Colla, S., *Boll. Soc. ital. biol. sper.*, 4, 298 (1929); *Chem. Abs.*, 23, 4496 (1929).

⁴⁷ Freytag, H., *Botan. Centr. Beihefte*, 51, 408 (1933); *Chem. Abs.*, 28, 504 (1934).

⁴⁸ Leonard, C. S., and Arthur, J. M., *J. Am. Pharm. Assoc.*, 23, 224 (1934).

⁴⁹ McCrae, A., *Science*, 71, 346 (1930).

⁵⁰ Conner, H. W., *Plant Physiol.*, 12, 79 (1937); *Chem. Abs.*, 31, 5017 (1937).

Results on the effect of ultraviolet rays on the changes in water, total and reducing sugars, and malic acid during the ripening of green-picked apples, peaches, pears and plums were irregular, according to Leoncini and Rogai.⁵¹ In some experiments, the total sugar was reduced (one-tenth to one-sixth) by irradiation.

Ultraviolet light (particularly of wave-length 2980A) causes browning of banana skins exposed in air but not in pure carbon dioxide. The effect is inhibited by hydrogen cyanide for wave-lengths less than 3200A, but the effect of the 3800A line is activated by a little hydrogen cyanide and inhibited by an excess. Enzymes of respiration may be involved in the effects.⁵²

⁵¹ Leoncini, G., and Rogai, F., *Ann. sper. agrar. (Rome)*, **21**, 108 (1936); *Chem. Abs.*, **31**, 8731 (1937).

⁵² Haussen, I., *Naturwiss.*, **26**, 136 (1938); *Chem. Abs.*, **32**, 6270 (1938).

Author Index

- Abbot, C. G.**, 1, 192, 196, 197, 714
Abderhalden, E., 670, 674, 675, 677, 709, 756, 766
Abe, G., 757
Abe, T., 764
Abel, E., 248, 447
Abelous, 432
Abrahamowicz, J., 657
Abram, H. H., 148
Ackerson, C. W., 814
Acly, H. E., 431
Adam, A., 793, 821
Adam Hilger, Ltd., 853
Adam, N. K., 804, 811
Adams, D. R., 763, 764
Adams, E. Q., 93, 738, 876
Adams, D. W., 460
Adel, A., 194
Aden, T., 369
Adkins, H., 805
Adler, E., 686
Atzelius, I., 358
Agarbiceanu, T., 273
Agduhr, E., 822
Agnew, M. C., 824
Agnew, R. G., 824
Agren, G., 689
Agulhon, H., 680
Ahier, G., 189
Ahrens, F., 601, 610
Ahrens, G., 810
Aicher, J., 142
Aickin, R. G., 291
Aikins, G. A., 761
Akiyama, M., 706
Akmatov, A. S., 869
Albanese, G., 646
Albela, D., 757
Albers, H., 683
Albers, V. M., 50, 271, 879
Albortal, M., 744
Albert Meyer-Sans Boeuf Co., 613
Alberts, H., 632
Albu, H. W., 355, 357
Albus, G., 742
Alekseevskii, E. V., 392, 460
Alexander, 100
Algerino, A., 647
Ali, M., 358
Alink, R., 648
Alius, H. J., 741
Allen, A. J., 72, 382, 674
Allen, E., 689
Allen, R. P., 248
Allenbach, 780
Allen, E. J., 155
Allingham, J., 662
Allison, F. E., 883
Allmand, A. J., 107, 108, 246, 252, 255, 284, 287-291, 297, 298, 346, 347, 357, 439, 441, 442, 443, 446
Almasy, F., 161, 314, 466, 473, 690
Almquist, H. J., 670, 856
Aloy, J., 407, 432, 525
Aloy, R., 525
Alpatov, D. M., 494
Alpatov, V. V., 717
Alphen, H. C., 35
Altenburg, J., 688
Alterthum, H., 47
Altschuller, M. M., 756
Alverdes, F., 684
Alvea, H. N., 356, 410
Amagat, P., 467
Amatore, G., 646
Ambroglio, A., 861
American Tobacco Co., 660
Ames, F. B., 836
Ammann, H., 364
Ammann Brass, H., 364
Ammon, R., 553
Amoureux, G., 671
Amiheim, F. J., 847
Amy, L., 188
Anand, H. L., 267
Andant, A., 108, 434, 456, 665
Anderson, A. K., 840
Anderson, C. N., 659
Anderson, E. G. E., 268
Anderson, G. M., 824
Anderson, H., 650
Anderson, J. A., 35, 40
Anderson, K. D., 461
Anderson, L. C., 476, 626
Anderson, N. J., 60
Anderson, P. G., 824
Anderson, R. J., 792, 795
Anderson, S. H., 46, 47
Anderson, W. R., 284
Anderson, W. T. Jr., 74, 79, 80, 97, 103, 105, 126, 131, 133, 135, 268, 340, 352, 636, 735
Ando, T., 817
Andraschko, E., 521
Andre, M., 516
Andrejeff, I., 299
Andresen, O., 835
Andresen-Kraft, C., 156, 171
Andrews, R. S., 661
Andrews, W. S., 38, 164, 189
Andrich, K., 182, 331, 545
Andrik, L., 759
Angeletti, A., 474
Angelica, V., 860
Angenot, P., 521
Anger, V., 519
Angström, A., 193
Ankus, T. C., 806
Ankinovich, A. G., 625
Antropoff, A. von., 366
Ansbacher, S., 852
Anschutz, 453
Anslow, G. A., 673
Anslow, W. P., 407
Anson, M. L., 676
Aoki, M., 350
Appel, W. D., 622, 636, 637, 638, 640, 642, 643
Appelmans, R., 711
Appleyard, E. T. S., 7
Appleyard, M., 429
Arago, F., 4
Ardenne, M. von., 142
Arend, A. G., 645
Arends, B., 425, 428, 437, 441, 458, 671, 674
Arens, H., 380, 381, 384
Ariga, T., 628
Arloing, S., 692
Armand-Delille, P., 770
Armour, R. W., 280
Armstrong, H. E., 497
Armstrong, R. T., 395, 466
Arnold, H. D., 49
Arnold, R. B., 723
Arnold, W., 695, 875, 881
Arnone, M., 57
Arnone, V., 57
Arnou, L. E., 629, 671, 674
Arnulf, A., 193
Arny, H. V., 657
Arons, 66
Arrhenius, S., 209, 377
Arrio, H., 630
Arthur, J. M., 712, 887, 889, 890
Arthus, M., 678, 691
Arwentiew, B., 494
Asada, T., 74, 116
Asahina, T., 670, 674
Asahina, Y., 506
Asami, Y., 40
Asano, K. D., 882
Asano, K., 601, 605, 606
Ashdown, A. A., 395, 466
Asher, D. W., 819
Ashkenaz, E. W., 760
Ashley, S., 280
Ashton, L. O., 841
Ashton, M. R., 682, 711, 716
Ashworth, J. R., 196
Askew, F. A., 511, 801, 804, 805, 806, 821
Asperger, H., 740
Astbury, W. T., 679
Asterblum, M., 629
Aston, F. W., 227, 366, 614
Astrovce, P. S., 847
Asundi, R. K., 53, 331
Aten, A., 206, 299
Athanasu, G., 105, 106
Athias, F., 405
Atkins, W. R. G., 103, 108
Atlas Electric Devices Co., 578
Atsuki, K., 617
Aubel, E. v., 293
Aubert, M., 467
Auchinachie, D. W., 818
Audubert, R., 101, 210, 339, 387
Auer, L., 558, 573
Auerbacher, I. J., 835
Augustine, J., 743
Auhagen, E., 805, 807, 821
Austen, R., 35
Austin, P. R., 548
Auwers, K. von., 500, 806, 810
Avakova, E. S., 652
Avery, W. H., 355
Avramenko, L., 243
Axilrod, B. M., 411
Axmann, 66, 74
Ayrton, Mrs. H., 46, 47
Ayyar, P. R., 541
Azuma, T., 124
Azuma, Y., 760
Azzi, A., 865
Baas-Becking, L. G. M., 881
Baba, H., 389
Babasaki, Y., 825
Babcock, H. D., 50
Bach, A., 868
Bach, H., 774
Bacharach, A. J., 785, 814
Bachem, A., 735, 739
Bacher, R. F., 27

- Bachhaus, A. A., 662
 Bachmann, P., 73
 Bachmann, W. E., 476, 477
 Bacu, A., 490
 Backer, H. J., 413
 Buckes, M., 416
 Bacon, H. E., 322
 Bacon, R. E., 443
 Badertscher, A. E., 658
 Badger, R. M., 280, 536
 Badische Anilin und Soda Fabrik, 173, 533
 Badoche, M., 423, 510, 511
 Badstübner, W., 425
 Badzynski, S., 513
 Bäckström, H., 178, 187, 356, 357, 422, 423, 473
 Baeder Illatszergyar R. T., 847
 Banninger, A., 415
 Bar, F., 851, 852
 Bär, R., 82
 Baeyer, A. von, 867
 Bagdasar'yan, K. S., 381
 Bagnall, H. H., 104
 Bahr, E. V., 297
 Bailey, A. A., 711
 Bailey, A. C., 709
 Bailey, C. H., 723, 830
 Bailey, K. C., 358
 Baird, 73, 78
 Baird and Tatlock, 103
 Baker, F. E., 659
 Baker, H. B., 286, 299, 376
 Baker, J. A., 888
 Baker, S. L., 711
 Bakker, H., 618, 872
 Balada, A., 655
 Balakhovskii, S., 740
 Balandina, V., 605
 Balard, A., 305
 Balderrey, F. C., 747, 753, 772
 Baldini, V., 474
 Baldwin, W. M., 764
 Balezin, P., 837
 Balinkin, I. A., 68
 Balis, S. F., 139
 Balmer, 20, 22
 Balsac, F. de, 817
 Baltes, J., 565
 Baly, E. C. C., 49, 152, 209, 214, 218, 228, 267, 268, 271, 287, 368, 866, 868, 869, 870, 882
 Bamberger, E., 496
 Bamberger, P., 821, 839
 Bamford, C. H., 422, 425, 429
 Ban, N., 829
 Bancel, J. des, 871
 Bancel, L. des, 585
 Bancroft, W. D., 248
 Bandel, G., 575
 Bandow, F., 665
 Banerjee, B. N., 856
 Banerjee, S., 682, 684
 Banerjee, T., 383, 387, 433, 447
 Banerji, R. C., 248, 249
 Banerji, S. N., 452
 Bang, S., 692, 693, 697, 700, 701
 Bannister, C. O., 661
 Banta, C., 481
 Bar, N., 81
 Barak, M., 301, 310
 Barak, K., 632
 Baratto, A., 710
 Barbier, D., 193
 Barenberg, L. H., 775
 Bargellini, G., 474, 482
 Barker, E. F., 194
 Barker, J., 582
 Barker, S. G., 633, 635, 636, 637, 642
 Barker, W. F., 287, 868
 Barkoff, S., 624
 Barkus, O., 747, 753
 Barkworth, H., 560
 Barnes, B. T., 93, 110, 144, 145, 190, 738
 Barnes, D., 673
 Barnes, D. J., 814, 834, 835
 Barnes, J., 153, 154
 Barnicoat, C. R., 643
 Batone, V. G., 760
 Barnett, F., 504
 Barr, D. F., 822
 Barr, G., 608, 613, 614
 Barral, P., 824
 Barrat, 724
 Barratt, S., 275, 368
 Barrett, H. J., 584
 Barritt, J., 623, 679
 Barrolier, J., 73
 Barsky, G., 354
 Barthen, C. L., 853
 Bartholomew, D. C., 772
 Bartlett, J. H., Jr., 317
 Barton, H. A., 325
 Barton-Wright, E. C., 868
 Bauishanskaya-Landsberg, F. S., 869
 Barve, P. M., 390
 Baryshnikova, A. N., 470
 Bassett, P. R., 51, 55
 Baskerville, C., 526
 Baskerville, M. L., 717, 764
 Bass, L. J., 518
 Bass, L. W., 362, 469, 702
 Basu, K., 540, 541
 Basu, K. P., 213, 487, 542, 548
 Basu, N. K., 854
 Batchelder, E. L., 835
 Bateman, J. B., 290
 Bates, F., 150
 Bates, F. J., 148
 Bates, J. R., 125, 150, 156, 243, 245, 257, 258, 289, 302, 303, 305, 318, 319, 344, 397, 414, 529
 Bates, P. M., 711
 Batley, A., 345
 Baudisch, O., 352, 362, 448, 449, 503, 518, 525, 882
 Bauer, K. H., 411, 565
 Bauer, W., 819
 Baumann, C. A., 846, 853
 Baumann, E., 205, 409
 Baumeister, W., 254, 864
 Baumgärtel, T., 720
 Baumgartner, J. G., 695
 Baumgartner, L., 822
 Bauminger, B., 436, 449
 Baur, E., 259, 339, 350, 362, 371, 441, 443, 445, 451, 512, 554, 556, 617, 856, 869, 873
 Baur, W. H., 486
 Bowden, F. C., 712
 Baxter, I. P., 612
 Baxter, R. A., 656
 Baxter, W. P., 327, 328
 Bay, Z., 156-158
 Bayerl, V., 746
 Bayle, F., 77
 Bayley, P. L., 188
 Bayliss, M., 51
 Bayliss, N. S., 244, 291
 Bayne-Jones, S., 693, 694, 698, 773
 Bazurina, E. N., 874
 Bazzoni, C. B., 694
 Beach, A. C. G., 381
 Beard, H. H., 804
 Beard, L. C., Jr., 656
 Beardslee, F. C., 829
 Beattie, J. M., 720
 Beatty, H. A., 473
 Beatty, W. A., 276
 Beau, S. Le, 601
 Beauverie, J., 706
 Beaver, J. J., 388
 Bechdel, S. L., 786, 790
 Bechtel, H. E., 790, 836
 Beck, A., 463
 Beck, A. B., 502
 Beck, H., 51, 742
 Beck, H. H., 843, 844, 845
 Beck, L. V., 860
 Beck, W. A., 888
 Becker, A. L., 36
 Becker, E., 580
 Becker, H., 69, 314, 330, 331
 Becker, J., 562, 571, 830
 Becker, J. A., 131
 Becker, J. P., 672, 678
 Becker, W., 612
 Becking, L. B., 669
 Beckley, V. A., 659
 Beckman, A. O., 43, 321, 323, 333
 Beckwith, T. D., 710
 Becquerel, E., 6, 269, 376, 381
 Bedford, C. W., 498, 527, 528, 640
 Bedford, E. F., 640
 Bedford, T. H., 695
 Bednarczyk, W., 432
 Bednyagina, N. P., 512
 Beebe, M. C., 648
 Beese, N. C., 149
 Beesley, E., 108, 284, 287, 290
 Beeson, W. M., 853
 Behmel, G., 518, 521
 Beil, A., 635
 Bekhterev, P., 444
 Beletskii, F. A., 194
 Bell, J., 870
 Bell, L., 763
 Belleaud, R. L. M., 73
 Bellenot, H., 248, 254, 445, 446
 Belloc, G., 790
 Bellot, M., 391
 Be Miller, L. N., 806
 Benard, 775
 Bénard, H., 688
 Bender, R. C., 839, 841, 844
 Bendix-Nielsen, I. B., 651
 Benedict, H. C., 268
 Benedict, H. M., 888
 Benedict, W. L., 653, 654
 Benedict, W. S., 394
 Benford, F., 143, 144, 146, 190, 193, 195, 197, 198, 200, 352, 781
 Bengtsson, F., 237
 Benjamin, H., 822
 Benjamin, M., 131
 Bennekou, I., 525
 Bennett, H. B., 785
 Bennholdt Thomsen, C., 759
 Benoit, 5
 Benrath, A., 346, 361, 396, 400, 511, 515, 529, 532, 540
 Benson, G., 421
 Benton, A. F., 441
 Bentzen, T., 643
 Benvenuto, E., 752
 Benz, F., 852
 Béranec, J., 486, 538
 Berchet, G. J., 411
 Bercezi, H., 365
 Beretta, U., 297
 Beretovskaya, F. I., 454
 Berg, W. F., 378
 Berge, K., 444
 Bergel, F., 544
 von Bergen, W., 622
 Berger, E., 176
 Berger, G., 368, 442, 444, 451
 Berger, G. W., 654
 Berger, L., 438
 Berger, W. E., 351
 Bergfeld, W., 777
 Bergmann, 23, 24
 Bergmann, E., 395, 403, 671, 672
 Bergmann, P., 316
 Bergmann, W., 817
 Bergstrom, F. W., 44, 320, 321, 349

- Berke, J. D., 824
 Berkeley, W. E., 48
 Berlemont, G., 78
 Bernal, J. D., 810
 Bernard, J. E., 693
 Bernauer, C., 868
 Bernd, E. C., 722, 829, 840
 Bernhard, A., 792, 825
 Bernhard, O., 769, 770, 778
 Bernhardt, F., 78, 366
 Bernheim, 784
 Bernheim, G., 663
 Bernheim, M., 780, 781
 Bernoulli, A. L., 432, 433
 Bernreuther, F., 287
 Bernstein, G., 597, 598
 Bernstein, P., 337, 425
 Berry, E. K., 151
 Berry, G. P., 712
 Berryhill, W. R., 823
 Berthelot, A., 671
 Berthelot, D., 206, 274, 281, 299, 310, 318, 322, 324, 330, 351, 359, 393, 402, 406, 408, 414, 416, 418, 422, 425, 428, 432, 433, 434, 435, 437, 440, 448, 456, 457, 458, 461, 462, 463, 466, 518
 Berthoud, A., 248, 254, 255, 259, 343, 344, 351, 404, 445, 446, 447, 480, 485, 486, 487, 488, 538, 541, 548, 549
 Bessemans, A., 757
 Besson, A., 534
 Bestucheff, 360
 Bethke, R. M., 787, 831, 838, 841
 Betz, H., 31
 Beuner, H., 793
 Beunes, A., 52
 Beutel, E., 589, 615, 678
 Beutler, H., 265
 Bevan, P. V., 282, 284
 Beyersdorfer, P., 432, 434
 Bhaduri, B., 516
 Bhagwat, W. V., 186, 188, 280, 364, 442, 446, 538
 Bhargava, L. N., 522, 883
 Bhargava, P. N., 250, 440
 Bhatnagar, S. S., 253, 267, 268, 358, 360, 390, 486, 698
 Bhatta, B., 447
 Bhattacharji, A. K., 337
 Bhattacharya, A. K., 210, 250, 251, 252, 260, 344, 345, 350, 364, 369, 371, 387, 434, 446, 447, 450, 452, 541
 Bhattacharya, S. C., 538, 548
 Bhattacharya, S. K., 450, 486, 538
 Biancani, E., 688
 Biancani, H., 688
 Bichowskaja, A., 776
 Bichowsky, F. R., 25, 241
 Bidot, E., 612
 Bidwell, S., 269
 Bie, 692
 Bielecki, J., 401, 416, 431, 435
 Bichlavi, V., 554
 Bier, O. G., 863
 Bierer, J. M., 607
 Bierry, H., 402, 433, 434, 851, 852, 871
 Biggs, G. D., 120
 Biagi, D., 499
 Bilek, F., 837
 Bilham, P., 831
 Billen, F., 366
 Billmann, A., 517
 Billon-Daguerrre, A. L., 124
 Bills, C. E., 716, 790-795, 797, 803, 805, 806, 807, 809, 813, 817, 820, 822, 823, 828, 832
 Biltz, H., 493
 Bincer, H., 621
 Bing, F. C., 846
 Bing, K., 610
 Bing, M., 722
 Binkley, S. B., 856
 Binks, 66
 Binz, A., 400
 Biquard, C., 405
 Biquard, D., 188, 454
 Birch, S. F., 413, 656
 Birch-Hirschfeld, A., 762
 Bird, L. F., 80, 105, 133, 135
 Birge, R. T., 163, 225, 227, 235, 282, 293, 308, 317
 Bischoff, M. A., 663
 Biswas, N. N., 350
 Biswas, S. C., 351
 Bittenbender, H. A., 175
 Bjerrum, N., 218
 Blacet, F. E., 419, 420, 421, 422, 424
 Black, A., 780, 788, 789, 791, 830, 839, 853
 Black, C. K., 385
 Black, N., 727
 Black, W. A., 716
 Black, W. C., 824
 Blackberg, S. N., 824
 Blackburn, P. W., 723, 728, 729
 Blackett, P. M. S., 229
 Blackie, K. G., 411
 Blackman, F. F., 873
 Blackman, S. S., Jr., 749
 Blair, G. W. S., 391
 Blair, J. M., 378, 380
 Blaisdell, C. A., 620
 Blake, G. G., 50
 Blake, G. J., 76
 Blake, H. D., 143
 Blake, J. T., 596
 Blanc, C., 530
 Blanchard, E. W., 759
 Blank, I. H., 695
 Blankensma, J. J., 496
 Blas, D., 775
 Bleqvad, O., 858
 Bliensdorfer, P., 689
 Bliss, A. R., Jr., 814
 Bliss, H. J. W., 548
 Blix, G., 822
 Bloch, B. M., 429
 Bloch, C. E., 751, 774, 779
 Bloch, E., 7
 Bloch, F., 372
 Bloch, L., 7, 167
 Blocher, L. M., 720
 Blochmzew, D., 374
 Blom, A. V., 564, 580
 Blum, G., 715
 Blum, H. F., 629, 760, 860, 862, 863, 864, 865, 866
 Blumberger, J. S. P., 624
 Blunt, K., 846
 Blunt, T. P., 692
 Boake, A., 545
 Boardman, R., 60
 Boas, 42
 Bocchi, C., 362
 Boek, F., 816
 Bockemüller, W., 440
 Bodenstem, M., 206, 207, 210, 211, 248, 251, 272, 274, 275, 276, 278, 279, 280, 281, 283, 284, 286, 287, 288, 289, 290, 297, 298, 305, 306, 307, 311, 312, 313, 314, 347, 505
 Bodforss, S., 493
 Bodnár, J., 868
 Boehm, E., 320
 Böhm, H., 297
 Böhm, H., 743
 Boer, A. G., 815
 Boer, J. H. de, 141, 372, 374, 479, 670
 Boeseken, J., 403, 404, 476, 564, 565
 Bottger, O., 518
 Bogdanova, G. P., 748
 Bogert, M. T., 423, 491
 Boggio-Lera, E., 366
 Bohr, N., 17, 21, 22, 163, 214, 218
 Bohstedt, G., 786
 Boissonas, C. G., 524
 Bokimik, Y. L., 381, 383
 Bol, C., 124
 Bolin, I., 449
 Boll, F., 857
 Boll, M., 107, 248, 369, 370, 443
 Bolland, J. L., 332, 596
 Bolley, D. S., 572
 Boltzmann, L., 15
 Bomskov, C., 754
 Bonacini, C., 663
 Bond, W. R., 268
 Bondy, H. F., 602, 603
 Bonhoeffer, K. F., 156, 214, 226, 230, 231, 242, 258, 272, 273, 275, 297, 302, 304, 317, 319, 320, 372, 393, 453
 Bonner, J., 850
 Bonnet, L., 346
 Bonnet, R., 681
 Bousignore, A., 849
 Bonsor, S., 723
 Booher, J. E., 272, 537
 Book, G., 544
 Boone, F. H., 783-785
 Booth, H., 307
 Booth, H. S., 124
 Booth, R. G., 817, 848
 Norden Co., 842
 Bordier, H., 127, 209, 293
 Borgeaud, P., 812, 832
 Borgwardt, E., 431, 514
 Born, M., 373
 Borocco, A., 367
 Borrows, P. J., 776
 Borsiewicz, A., 754
 Borstler, E. W., 35
 Boshell, G., 678
 Bosthamley, R. P., 355
 Bott, J., 46
 Bottomley, 73, 78
 Bottomley, J. F., 151
 Bouchard, J., 390
 Boudlyne, G. F., 748
 Bourdillon, R. B., 798, 800, 801, 803, 806, 821
 Bourguet, M., 412
 Bouse, V., 523
 Bousquet, E. W., 548
 Bousset, R., 480
 Boutaric, A., 390
 Bover, J. R., 386
 Bovet, D., 860
 Bovie, W. T., 71, 72, 77, 674, 696, 698, 716, 758, 789
 Bovis, P., 275, 345
 Bowden, F. P., 339, 808, 848, 849, 854, 856
 Rowden, S. T., 626
 Bowen, E. J., 187, 216, 246, 247, 261, 298, 307, 328, 329, 347, 348, 404, 417, 418, 422, 423, 425, 426, 428, 430, 474, 475, 477, 509
 Bowen, I., 7
 Boyce, J. C., 293
 Boyd, H. T., 531
 Boyd, M. J., 862
 Boyer, J., 513
 Boyle, E., 855
 Brahender, C. W., 45
 Brackett, 20
 Brackett, F. P., Jr., 43, 104, 524
 Brackett, F. S., 873
 Bradford, 763
 Bradshaw, F. C., 330
 Bradshaw, H., 592, 609
 Brady, M. J., 814, 834
 Brady, O. L., 494
 Brachmer, F., 292, 299

- Bragg, W., 8
 Bragg, J. H., 841
 Bramhall, E. H., 46, 48
 Branchen, L. E., 588
 Brand, K., 550
 Brand, T. von, 822
 Brandt, A., 62
 Brandt, K., 630, 686, 689, 703, 818
 Branson, H. D., 814
 Brannigan, P. J., 343
 Braselton, C. H., 139
 Brattiano, S., 822
 Brattain, W. H., 93
 Brauchli, E., 796, 833
 Brauer, G., 346
 Braun, E., 266, 432
 Brauner, L., 669
 Brauner, M., 669
 Braunsdorf, K., 556
 Brautigam, 452, 482
 Bravo, G., 636, 640
 Brawn, G., 758
 Braz, J. le, 169
 Brdicka, R., 368
 Breadner, R. L., 142
 Bredig, G., 64, 315, 339, 416, 449, 516
 Breguet, A., 588
 Bremer, K., 490
 Brenard, G., 320
 Bienschede, W., 313, 346, 394
 Brewer, A. K., 31, 327
 Brewster, C. M., 481
 Brice, B. A., 240
 Brickwedde, F. G., 385, 386, 793, 803
 Briers, F., 254, 255, 279, 446
 Brieger, G., 680
 Brigando, J., 670
 Briggs, G. E., 872, 875, 876
 Briggs, J. A., 856
 Briggs, S., 362
 Brillouin, L., 374
 Briner, E., 62, 533
 Brings, T., 319
 Brinkman, H., 52
 Brintzinger, H., 679
 Briot, A., 349
 British Celanese, Ltd., 173, 411, 585
 British Hanovia Co., Ltd., 129
 British Medical Research Council, 846
 British Thomson-Houston Co., Ltd., 138, 143, 146, 150
 Britton, E. C., 531
 Broadbent, H. S., 723
 Brock, G. C., 178
 Brocklesby, H. N., 574
 Brockmann, H., 816, 817
 Brocq-Rousseau, D., 860
 Brode, W. R., 163, 368, 373, 624, 642, 643
 Brodmann, L., 282, 474
 Bromley, H. A., 619
 Brons, F., 308
 Brooks, B. T., 527, 530, 531, 653
 Brooks, L. M., 789
 Brooks, S. C., 669
 Brophy, J. J., 650
 Brose, H., 228
 Brosset, C., 367
 Brotzu, G., 758
 Brougher, J. C., 819
 Bioux, G. C., 354
 Brown, A., 170, 782, 837
 Brown, A. G., 307
 Brown, E. B., 699, 700
 Brown, F., 885, 887, 889
 Brown, G., 829
 Brown, H., 756
 Brown, H. T., 875
 Brown, H. W., 712, 731
 Brown, M., 639
 Brown, R. A., 645
 Brown, W. B., 574
 Brown, W. G., 237, 273, 275
 Brown, W. H., 754
 Brown, W. L., 31
 Browning, C. H., 693, 694, 697, 706
 Brownscombe, E. R., 209
 Bruce, H. M., 801, 805, 806, 820, 821
 Bruce, P. L., 596
 Bruchhaus, E., 343, 369, 370
 Bruck, E., 746
 Brückersteinkuhl, K., 571
 Bruckner, J., 817
 Brüll, W., 359
 Bruere, A. de la, 651
 Brucce, S., 720
 Brulat, G., 266, 354, 450, 463
 Bruijn, H. de, 254, 264, 864
 Bruijnes, J., 132
 Bruner, E., 621
 Bruner, L., 443
 Brunken, J., 812
 Brunner, K., 657
 Brunner, O., 857, 858
 Bunschwig, R., 656
 Brunschwitz, A. M., 385
 Bruylants, P., 458, 550
 Bruzau, Mme., 494
 Bryant, W., 217
 Ruadze, S., 677
 Buchanan, E. B., 721
 Buchanan, G. H., 354
 Buchwald, K. W., 803
 Buda, G. de, 645
 Budde, 610
 Budde, E., 282
 Buchi, P. F., 439, 443, 869
 Bulow, M., 849
 Bungeles, W., 865
 Bungei, H., 836
 Bugarski, S., 538
 Bugyi, B., 689
 Buhtz, E., 832
 Bunsov, B. V., 612
 Bunson, H., 5, 97, 107, 121, 192, 193, 195, 197, 198
 Bulgakosa, S. P., 849
 Bulch, P. K., 495
 Bundesen, H. N., 170, 173, 196
 Bungartz, E., 172
 Bunker, J., 268, 727, 781, 835
 Bunker, S. W., 660
 Bunn, C. W., 404
 Bunsen, R., 18, 205, 206, 271, 285
 Butaway, A., 809
 Burdick Corporation, 58, 126, 127
 Bureau of Standards, 165, 169, 174, 180, 189, 579, 661, 644
 Buige, E. L., 685
 Burge, W. E., 685, 689, 752, 763
 Burger, G., 694
 Burger, H. C., 96
 Burgess, C. H., 285
 Burgess, R., 727
 Burghardt, C. A., 601
 Burgher, K., 259, 260
 Burk, D., 869, 883
 Burke, K. A., 398
 Burke, R. E., 804
 Burkholder, F. R., 887
 Burns, G. R., 449, 873, 876
 Burns, K., 50
 Burns, L., 34, 97, 111-114, 177
 Burroughs, R. E., 382
 Burt, J. R., 362
 Burton, H. B., 784
 Burton, M., 244, 438, 439, 459, 460
 Buruain, L., 849
 E. A. Busch A.-G. Optische Industrie, 167
 Buschke, A., 744
 Busse, A., 816
 Busse, P., 808, 810, 821
 Busse, W. F., 328
 Bussmann, G., 740
 Butaeva, F., 93
 Butenandt, A., 689, 817
 Butironi, C., 291
 Butkov, K., 238, 342
 Butler, A. M., 839
 Butler, C., 509
 Butler, L. W., 556
 Buttolph, L. J., 66, 75, 76, 80, 85, 89-92, 117, 130-132, 143, 182, 259
 Cabannes, J., 193, 297
 Cadenhead, A., 391, 421
 Cady, W. G., 49
 Cady, W. H., 614, 635, 637, 640
 Cahon, M. H., 784
 Calabek, J., 695
 Calame, A., 743
 Calcagni, G., 354, 883
 Calgano, O., 815
 Califano, L., 685
 Callahan, M. J., 589
 Callo, A., 167, 563, 663
 Callow, R. K., 806, 809, 820, 821
 Cambi, L., 624
 Cameron, A. E., 383
 Cameron, F. K., 504
 Cameron, J., 708
 Camp, J. P., 5
 Camp, W. H., 872
 Campbell, A. N., 64
 Campbell, A. W., 612
 Campbell, F. L., 659
 Campbell, I. A., 744
 Campion, J. E., 836
 Campsie, H. G., 829
 Camus, 775
 Candler, A. C., 25
 Cannon, C. Y., 835, 838
 Cannon, H. J., 846
 Cantieni, R., 402-404, 422, 432, 433, 440, 521
 Capper, N. S., 504, 511, 854
 Carbide and Carbon Chemicals Corp., 410
 Carboxyhyd. A.-G., 870
 Carreddu, G., 754, 755
 Carey-Lea, 376
 Carey, G., 190, 257
 Carl, 885
 Carls, H., 766
 Carlsohn, H., 337
 Carlson, W. W., 345
 Carlton, M., 299
 Carmichael, E. B., 690, 718
 Carnielli, P., 749
 Carnot, 775
 Cao, M. de, 813
 Carothers, W. H., 411, 415
 Carpenter, A. W., 608
 Carpenter, J. A., 653
 Carr, C. J., 658
 Carr, E. P., 394, 413
 Carr, F. H., 539
 Carrick, C. W., 814
 Carrico, J. L., 401, 535
 Carroll, B. H., 627
 Carroll, M. J., 708
 Carruthers, J. E., 422
 Carst, A., 156
 Carter, C. W., 863
 Carter, H. D., 64
 Carter, H. E., 541
 Cartland, G. F., 822
 Cartledge, G. H., 444, 445
 Cartwright, C. H., 96, 466
 Carvalho, A. P. de, 268, 493, 521
 Carver, W. L., 613
 Carwile, L., 326
 Casparis, H., 783

- Casperson, T., 704
 Cass, O. W., 534
 Cassel, H. W., 452
 Cassidy, H., 828
 Castagna, S., 756
 Castelain, L., 722
 Castellini, P., 849
 Castiglioni, A., 468, 511, 521, 623
 Castille, A., 394, 401, 458, 504, 506, 798
 Castle, D. C., 854
 Catel, W., 782
 Cathala, J., 285, 286, 288, 311, 313
 Cautjolle, F., 523
 Caylor, H. P., 861
 Cazzini, U., 679
 Cecelsky, J., 504
 Cekada, E. B., 684
 Celluloid Corporation, 173
 Cernovodeanu, P., 693, 720
 Ceruti, G., 752
 Chabre, P., 853
 Chacrabarti, S. N., 559
 Chadwick, S., 69, 292, 293, 307
 Chakravarti, D. N., 629
 Chakravarti, G. C., 624
 Chakravorty, P. N., 851
 Chakravorty, S. K., 236
 Chakrohortu, B., 239
 Chalkley, L. Jr., 268
 Chalmers, W., 584
 Chalonge, D., 156, 157, 163, 193, 297
 Champion, C. H., 51
 Champion, C. H., and Co., Ltd., 51
 Chance Bros. & Co., Ltd., 164, 167, 169
 Chance, W. H. S., 164
 Chaney, N. K., 52, 829
 Chapman, A. G., 872
 Chapman, A. T., 532
 Chapman, D. L., 69, 253-255, 279, 285, 288, 289, 292, 293, 307, 311, 446
 Chapman, J., 776
 Chapman, M. C. C., 287
 de Chardonnet, 762
 Charlampowiczowna, B., 501
 Charlton, F. B., 714, 890
 Chase, A. M., 857, 859
 Chassard, 784
 Chastang, P., 255, 360
 Chattaway, F. D., 474, 497
 Chatterjee, H. K., 485
 Chatterji, A. C., 377
 Chatwin, J. E., 404
 Chaux, R., 511
 Cheesman, G. H., 332
 Chemische Fabrik Buckau, 611
 Chen, Y. H., 817
 Cherdumtzev, S., 383
 Cherrington, V. A., 777
 Cherry-Burrell Corporation, 844
 Chertoff, G. J., 610
 Chesley, A. L., 660
 Chesney, J. W. D., 58, 81, 828, 840
 Chesnokov, V., 874
 Cheunz, W. M., 348
 Chevallier, A., 689, 853, 855, 856
 Cheymol, J., 754
 Chichester, D. F., 856
 Chick, H., 789, 836
 Chieff, G., 477
 Chik, W., 414
 Child, R., 493
 Chilowsky, C., 105
 Chin, T. L., 860
 Chinchin, I., 586, 619
 Chisholm, C., 785
 Chmura, T., 357
 Chocetta, A., 863
 Chronon, Y., 853, 855
 Chorozak, T., 742
 Choucroun, N., 631
 Choudhri, R. S., 887
 Choun, C. K., 825
 Chovin, P., 510
 Chow, B. F., 865
 Chow, T.-C., 330
 Chretien, A., 370
 Christen, C., 684
 Christian, W., 687, 688, 853
 Christiansen, J. A., 276
 Christison, F., 34, 143, 194-197
 Christy, A., 329
 Chu, T. C., 414
 Church, A. E., 855
 Church, H. F., 608
 Ciamician, G., 393, 449, 468, 470, 474, 476, 491, 493, 496, 511, 515, 517
 Ciechowski, L., 294
 Ciusa, R., 494
 Ciusa, W., 555
 Claffin, D., 819
 Claman, I., 819
 Clar, E., 504-506, 511
 Clark, A. B., 858
 Clark, G. L., 43, 209, 572, 593, 663
 Clark, J., 104, 170, 675, 733, 740, 748, 775, 784
 Clark, L. H., 111, 798
 Clark, W., 379
 Clark, W. M., 621
 Clarke, H. T., 183
 Claude, A., 36
 Claus, G., 142
 Claus, W. D., 707, 768
 Clausen, S. W., 825
 Clement, L., 463
 Clewell, I. H., Jr., 591
 Clifton, C. E., 860
 Cline, J. F., 330
 Clover, G. R., 586
 Clusius, K., 332
 Cluzet, I., 391, 756, 885
 Coade, E. N., 170, 173, 196
 Coherentz, W. W., 34, 50, 57, 96, 97, 99, 106, 107, 109, 127, 128, 144, 146, 147, 165, 166, 174, 175, 183, 188, 194, 195, 198, 200, 201, 377, 694, 695, 711, 738
 Cochran, R. L., 175
 Coe, M. R., 560, 561, 611
 Coc, W. S., 209
 Coehn, A., 69, 182, 246, 253, 272, 274, 275, 281, 286, 299, 308, 314, 318, 330, 331, 339, 529
 Cofman, V., 592
 Cohen, F. H., 852
 Cohen, I., 772
 Cohen, W. D., 403, 404, 476, 477
 Cohn, B. N. F., 818
 Cohn, C., 670
 Cohn, W. M., 35, 156
 Colange, G., 295
 Colby, W. F., 227
 Cole, A. F. W., 283
 Cole, V. V., 822
 Colebrook, D., 776
 Colebrook, L., 775, 776
 Colefax, M. A., 173
 Coleman, C. H., 531
 Coleman, I. J., 380
 Colgate-Palmolive-Peet Co., 743
 Colla, S., 888, 890
 Collazo, J. A., 822
 Collens, W. S., 774
 Collier, H. B., 680, 683, 684
 Collin, A., 476
 Collinet, M., 273
 Collins, H., 691
 Collip, J. B., 819
 Colman, H. C., 816
 Colthoff, P. J. G., 411
 Coltman, R. W., 51
 Columbo, G., 621
 Cornel, M., 819, 824
 Committee on Photochemistry, National Research Council, 96
 Common, R. H., 819
 Compagnie des Lampes, 142, 179
 Compagnie Lorraine de Charbons pour l'Electricité, 51
 Comptoir des textiles artificiel, 617
 Compton, A. H., 8, 9, 25
 Compton, K. T., 31, 47-49, 81-83, 93
 Conant, J. B., 421, 489, 878
 Condon, E. U., 163, 235
 Condorelli, F., 861
 Cone, L. H., 626
 Conklin, E. P., 545
 Conner, H. W., 890
 Connerade, E., 478, 547
 Conrad-Billroth, H., 271, 416, 467, 469, 479
 Conradty, E., 58
 Conradty, O., 58
 Consortium für Elektrochemische Industrie, 422
 Continental Caoutchouc and Gutta-Percha Co., 652
 Cook, A. H., 500
 Cook, G. A., 305, 344
 Cook, J. W., 504
 Coolhaas, C., 710
 Coolidge, W. D., 803
 Cooper, 773
 Cooper, C. A., 81
 Cooper-Hewitt, P., 66, 76, 77
 Cooper-Hewitt Electric Co., 72, 80, 650
 (see also General Electric Vapor Lamp Co.)
 Coper, K., 383
 Corbet, A. S., 350, 351
 Cornière, J., 271, 326
 Cordes, H., 275, 282, 330, 529, 530
 Correa, L., 669, 803
 Cornille, T., 742, 849
 Cornelius, F., 293
 Cornil, L., 689
 Corning Glass Works, 142, 165, 169, 172, 173
 Cornu, M. A., 7, 78, 192, 195
 Cornubert, R., 516
 Corson, W. C., 825
 Cortese, D., 555
 Cossu, F., 676
 Costa, R. M. da, 491
 Coster, D., 308, 447
 Coster, J. H., 831
 Cotton, A., 266, 383
 Coulon, A. de, 766
 Coulsen, E. A., 489
 Coulter, C. R., 670
 Coulter, J. S., 770
 Coulter, M. D., 724
 Council of Physical Therapy, American Medical Association, 769
 Courmont, J., 127
 Courtman, H. R., 515
 Cousin, E., 683
 Coward, K. H., 789, 790, 791, 802, 817, 819, 837, 853
 Cowdry, E. V., 822
 Cowen, R., 846
 Cowper, W., 647
 Cox, G. I., 772
 Cox, S. J., 853
 Cox, W. M., Jr., 797, 803, 805
 Craciunescu, E., 472
 Craggs, H. C., 288, 289, 291
 Craig, F. N., 882
 Craig, J. D., 834
 Craig, P., 146
 Cramer, F., 279

- Cramer, H., 741
 Cramer, W., 748
 Crary, R. W., 401
 Cravath, A. M., 83
 Creach, P., 683
 Creamery Package Manufacturing Co., 844
 Creighton, H. M., 722, 829, 840
 Cremer, E., 288, 298, 302
 Cremer, W., 687
 Crespi, E., 633
 Crespi, M., 310
 Crew, H., 3, 49
 Crews, S. K., 94, 95, 109
 Crews, S. K., 853
 Crichton, J. A., 786
 Cricks, Rigby and Rigby, Ltd., 60
 Crimm, P. D., 818, 823, 824
 Crist, J. W., 848
 Crist, R. H., 121, 122, 170, 172, 344, 357, 358, 881
 Croad, A. K., 100, 105
 Crockford, H. D., 354
 Crofts, E., 744, 745
 Croll, P. R., 586
 Crone, H. G., 425-427, 430, 431
 Crounheim, G., 742
 Crook, W. J., 662
 Crookes, W., 164
 Cropp, W., 367
 Cross, C. L., 176
 Crowe, M. O' L., 690
 Crowfoot, D., 810
 Croxatio, H., 819
 Croze, A. B., 723
 Crozier, R. N., 411
 Cruikshank, W., 284
 Crumpler, C. J., 461
 Cuccudoro, M., 651
 Cultrera, R., 353, 849
 Cumming, W. M., 493, 499, 503
 Cunliffe, P. W., 128, 346, 615, 623, 633, 636, 638
 Cunningham, E. L., 657
 Cunningham, G. L., 441
 Cunningham, H. L., 853
 Cunningham, I. J., 818
 Cunningham, J. P., 464
 Cuny, L., 832, 840
 Curie, M., 708
 Curme, G. O. Jr., 411
 Curry, J., 882
 Curtis, H. A., 340, 345, 634
 Custis, H. H., 471, 522, 540, 553
 Custers, J. P. H., 479, 495, 670
 Cuzin, J., 860

D
 Dacheux, P., 656
 Dachlauer, K., 532
 Dadiou, A., 224
 Dandiez, J., 293
 Daehn, E., 492
 Dahm, T. M., 177
 Bailey, H. T., 268
 Dain, B., 104, 341, 452
 Dainton, F. S., 461
 Daire, P., 720
 Daland, G. A., 674, 716
 Dale, H. H., 819, 821
 Dale, M. L., 823
 Dalen, G., 643
 Dalmer, O., 814
 Damon, G. H., 426, 427
 Dana, D. W., 76, 92
 Danckworth, P., 167, 663
 Dane, H. R., 885
 Danelli, J. F., 811
 Dangeard, P. A., 871, 888
 Daniels, A. L., 789, 830
 Daniels, F., 122, 190, 209, 210, 326-328, 426, 427, 486, 535, 802-804, 813, 876
 Danilov, A. N., 873
 Dahn, A. T., 489
 Dann, W. J., 555, 854
 Dannmeyer, F., 846
 Darrow, K. K., 40, 47
 Dartnall, H. J. A., 857
 Darwin, C. G., 17
 Das, N., 689
 Dastur, N. M., 856
 Dastur, R. H., 873, 874, 877, 882
 Datta, A. K., 272, 275
 Datta, S., 239
 Daugherty, K., 716
 Daube, P., 275
 Dauvilliet, A., 193, 209
 Davey, W. P., 591
 David, W. T., 209
 Davidovitch, P., 168
 Davidshofer, F., 877
 Davidson, D., 518
 Davidson, D. L., 823
 Davidson, J. G., 579
 Davies, A. C., 156
 Davies, D. R., 821
 Davies, E. C. H., 391
 Davies, J. B., 869
 Davies, J. S. H., 549
 Davies, L., 139
 Davies, W., 476, 489
 Davies, W. L., 561
 Davis, C. C., 607
 Davis, G. E., 750
 Davis, L., 711, 726
 Davis, M. E., 691
 Davis, N. W., 293
 Davis, R. F., 655
 Davis, T. L., 266
 Davis, T. W., 459, 460
 Davis, W. S., 721
 Davisson, C., 11
 Davy, H., 50, 310
 Davydov, B. I., 31
 Dawsey, L. H., 303, 327, 339
 Dawson, L. H., 94, 109, 160, 299, 338
 Dawson, T. R., 610
 Daynes, H. A., 608
 De, N. K., 854
 Deady, W. F., 638
 Dean, H., 578
 Dean, R. S., 524
 Deb, S., 240
 De Broglie, H., 10, 26
 de Bruijn, H., 254, 264, 864
 Debye, P., 17
 Deck, W., 271
 Decourt, J., 756
 Dede, L., 387
 Dedichen, H., 514
 Decey, I. J., 644
 De Fazi, R., 432, 477, 492, 511, 517, 710, 826, 885
 Deforge, A., 651
 Defries, R., 599, 605
 Degea, A.-G., 165
 Degkwitz, R., 821
 Degos, R., 756
 Deichsel, S., 659
 Dejardin, G., 193
 de Jonghe, A., 511
 Dejust, L. H., 818, 824
 Dekking, A. C. B., 474
 De Kowalski, J., 41, 156
 Delaplace, R., 798, 804
 Delf, E. M., 715, 885
 Dell Aquila, A., 755
 Delore, P., 559
 Demarest, R., 816
 Demina, E. N., 591
 Deming, L. S., 193
 Demo, M., de, 516
 de Monceiz, A., 209
 Demoussy, E., 715, 887
 Denes Goetz, J., 793
 Denham, A. F., 587, 590
 Den Hoed, D., 679
 Dennington, A. R., 723
 Dennison, D. M., 224, 226
 Denstodt, O. F., 574
 Depew, H. A., 607
 Deppe, M., 806, 810, 816
 Derbas, D., 756
 Dérèbere, M., 556, 619, 620, 624, 635, 663, 665
 De Rienzo, A., 819
 De Right, R. E., 399, 537
 Derow, M. A., 856
 Derrrett-Smith, D. A., 624
 Desai, B. L., 877
 Desai, R. N., 390
 Desai, M. S., 238, 239
 Desai, S. V., 350
 De Sanctis, A. G., 834, 841
 Desavitsch, E. C., 824
 Deshailliet, J., 62
 Des Bancelis, J., 871
 Des Bancelis, L., 585
 Descamps, R., 450
 Deschwander, J. von, 751
 Descombes, F., 727
 Desha, L. J., 665
 Deslandres, H., 218
 Desmurs, G., 651
 de Swietochowski, H., 772
 Deutsch, H., 819, 822
 Deutsche Gasglühlicht Auer-Ges., 172
 Deutsche Spiegelglas A.-G., 166, 167, 171
 De Vaney, G. M., 814
 Devers, P. K., 139, 151
 Dewar, J., 35, 294
 Dewey, L. H., 103, 356, 364, 443
 De Wolf, C. E., 885
 Dey, B. B., 488, 503
 Deysher, E. F., 558
 Deželich, M., 872
 Dhar, N. R., 188, 193, 194, 210, 247-253, 259, 260, 290, 299, 337, 344, 345, 350, 351, 357, 364, 371, 432, 434, 440, 442, 445-447, 450, 452, 522, 538, 541, 553, 559, 629, 673, 826, 867, 869, 870, 874, 883
 Dhéce, C., 698
 Diacono, H., 758
 Di Archangel, N., 660
 Dickerson, T., 387
 Dickhauser, E., 411
 Dickinson, R., 494
 Dickinson, R. G., 43, 258, 295, 306, 319, 321, 323, 327, 328, 336, 344, 347, 363, 371, 400, 401, 446, 534-536
 Dieke, G. H., 272, 416
 Dieffenbacher, K., 376
 Diehl, F., 759
 Dienert, F., 370, 720
 Dieterle, W., 183
 Dietsch, W., 600
 Dietz, E. M., 878
 Dietzel, R., 449, 493
 Digby, W. P., 580
 Dillman, L. M., 432, 703, 826
 Dillon-Weston, W. A. R., 711
 Dilthey, W., 647
 Dimroth, 808
 Dimroth, K., 795, 796, 809, 810, 812
 Dingee, A. L., 34
 Dingle, H., 192
 Dingwall, A., 495, 564
 Dinjasky, K., 515
 Dinsley, A., 650
 Doppel, C. J., 495, 670
 Di Renzo, F., 681
 Disch, J., 68
 Discherl, W., 421, 451, 670
 Dithmar, K., 805, 807
 Dittmar, R., 598-600, 610
 Ditto, Inc., 645

- Dittrich, E., 463
 Ditz, H., 615
 Ditzler Co., 587
 Dixon, H. H., 872
 Dixon, J. K., 317, 321
 Djang, T. G., 444
 Doan, F. J., 563
 Doan, G., 46, 49
 Dobbie, J. J., 249
 Dobrokhotova, E., 865
 Dobson, G. M. B., 193
 Dock, E. H., 608
 Dodds, E. C., 785
 Dodge, J. K., 721
 Doerflinger, 591
 Döring, B., 873
 Doering, U. W., 131
 Dogadkin, B., 593, 602, 605
 Dognon, A., 862
 Doisy, E. A., 856
 Doktorsky, A., 742
 Dolk, H. E., 873
 Doll, J. H., 346
 Dolls, M., 814
 Donat, H., 472
 Donat, K., 257
 Doniach, I., 865
 Donnan, F. G., 398
 Donovick, S. E., 710
 Dooley, D., 144
 Doiran, W., 354
 Dorcas, M. J., 50, 51, 55, 57, 60, 96, 101, 659, 829, 839, 841-844
 Dorée, C., 614
 Dorfman, M., 520
 Dorgelo, H. B., 271
 Dornic, P., 720
 Dorno, C., 99, 195
 Dorsey, N. E., 5
 Dote, S., 585
 Douglas, S. D., 411
 Douglass, E., 856
 Doull, J. A., 775
 Dove, 156
 Dove, W. F., 788
 Dow Chemical Co., 64, 531
 Dow, O. D., 839, 846, 848
 Downes, A., 692
 Downes, A. C., 53, 198-200
 Downs, C. R., 504
 Dowsing, 66
 Dozier, C. C., 188
 Dozois, K. P., 704
 Dragulescu, C., 467
 Draibach, F., 172
 Draibach, H., 172
 Drake, T., 814, 830, 837
 Draper, J., 205, 284
 Dreinhöfer, R., 482
 Dreker, I. J., 792
 Drew, A. H., 748
 Dreyer, G., 717
 Dreyfus, C., 173, 592
 Dreyfus, H., 411
 Dreyfus-Sée, G., 761
 Drigalski, W. von, 740
 Drukes, O., 267
 Drinker, P., 782
 Drucker, P., 755
 Drucker, S. V., 559
 Drummond, J. C., 789-791, 816, 831, 853, 855, 856
 Druyvesteyn, M. J., 131
 Dry Milk Co., 840
 Dryco Co., 842
 Duibe, H. L., 442
 Duhois, R., 59, 819
 Dubouloz, P., 433, 670, 742, 761, 855
 Du Bridge, L. A., 269
 Dubrisay, R., 354, 400
 Duce, W., 679
 Duclaux, 692
 Duclaux, J., 194, 381, 588
 Dürken, B., 765
 Düsing, W., 169
 Dufay, J., 193, 297
 Dufestel, L. G., 762
 Duffau, R., 818
 Duffendack, O. S., 160, 308
 Dufford, R. T., 464
 Duffraisse, C., 423, 508-511, 608
 Duggan, F. W., 411, 412
 Duggar, B. M., 708, 714, 732, 876, 885
 Duguid, J. B., 821, 822
 Duhme, E., 366
 Dujarric de la Rivière, R., 758
 Dumas, M. J., 615
 Duncan, A. B. F., 317, 322, 324, 394, 428
 Duncan, C. W., 790
 Duncan, D. C., 591
 Duncan, J. A., 159
 Dunicz, B. L., 501
 Dunlop Rubber Co., Ltd., 611
 Dunn, F. P., 494
 Dunn, J. T., 502
 Dunn, M. S., 670
 Dunnichiff, H. B., 358, 445, 448
 Dunning, F., 743
 Du Nôuy, P. L., 555
 E. I. du Pont de Nemours & Co., 411, 530, 534, 548, 562, 584, 591, 834
 Duquenois, P., 487
 Duret, G., 722
 Duceuil, E., 479, 797
 Durrant, G. G., 351
 Dushinskii, F., 244
 Dushman, S., 30, 47, 94, 131
 Dutcher, R. A., 780, 791, 814
 Duthell, J., 297
 Duthell, M., 297
 Dutoit, 344
 Dutt, S., 497, 624, 632
 Dutta, A. K., 240, 324, 330, 338, 354
 Dutton, H. J., 887
 Dux, W., 286, 287
 Dwight, C. H., 695
 Dworski, M., 706
 Dwyer, C. M., 708
 Dyche-Teague, F. C., 611
 Dydzyński, A., 393
 Dye, J. A., 781, 787
 Dye, M., 848
 Dyer, F. J., 853
 Dyer, J., 614
 Dykstra, H. B., 408, 591
 Dykstra, K., 513
 Dymond, E. G., 230, 231, 272
 Dyson, G., 311
 Dziedzicki, N., 95
 Dziewulski, H. v., 82
 Earle, W. R., 750
 Easley, M. A., 110, 144
 Eastman Kodak Co., 369, 382, 485, 588, 592, 621
 Eastwood, E., 416, 424
 Eberlin, L. W., 369, 382
 Ebersson, 773
 Ebersson, F., 696
 Ebert, L., 337
 Eccles, J., 188
 Eck, J. C., 813
 Eckart, C. H., 81
 Ecker, E. F., 684
 Eckert, A., 467, 506
 Eckert, F., 174
 Eckler, C. R., 853
 Eckstein, A., 779, 780
 Eckstein, H. C., 676
 Eddington, A. S., 191
 Eddy, C. E., 662
 Eddy, W. H., 839
 Eder, J. M., 168, 248, 361, 365, 627, 743
 Ederer, S., 753
 Edge, S. R. H., 618
 Edgerton, H. A., 379
 Edisbury, J. R., 555, 853, 856
 Edleson, N. E., 157, 158
 Edlén, B., 7, 42
 Edwards, N. J., 447
 Edwards, T. G., 306
 Eeckhout, J., 351
 Eeklen, M. van, 852
 Eerola, L. V., 849
 Ehmov, A., 865
 Ehmov, W. W., 865
 Egeler, C. E., 144, 147
 Eggert, J., 209, 377, 378, 381, 384, 454, 455, 544, 562, 624
 Eggleton, J., 849
 Egidi, E., 754
 Eggle, K., 888
 Egloff, G., 652-654
 Egyesült Izzólampa és Villamos-sági, R. T., 124
 Ehrenstein, J., 451
 Ehrismann, O., 704
 Ehrmann, K., 401, 413
 Eibner, A., 384, 385, 556, 564-566, 572, 574, 581, 663
 Eichelbaum, G., 688
 Eichelberger, M., 745
 Eichler, A., 621
 Eidinow, A., 101, 102, 179, 734, 741, 775, 861
 Eigenberger, E., 413
 Eiman, J., 836, 842
 Einstein, A., 17, 191, 207, 269, 342, 355
 Eisenberg, K. B., 170
 Eisenbrand, J., 271, 337, 351, 479, 658
 Eisenschimmel, W., 105
 Eising, E. H., 727
 Eisler, M. v., 873
 Eissner, W., 679
 Ekeley, J. B., 481, 515
 Elbe, G. v., 304, 305
 Elbs, K., 357, 504
 Elder, H. M., 407, 548
 Eldred, B. E., 533
 Eldridge, J. A., 16
 Elektrizitätswerk Louza, 591
 Elenbaas, W., 84, 93, 124, 135, 149, 150, 171
 Eley, D. D., 262
 Elgin, J. C., 322, 323
 Elhart, W., 402
 Elias, O. A., 830
 Elason, R. T., 770
 Ellenbogen, V., 776
 Fillett, A., 150
 Ellingboe, E., 492
 Ellinger, F., 670, 672, 673, 740, 741
 Ellinger, P., 794, 851
 Ellington, E. V., 835
 Elliott, A., 282
 Elliott, E. L., 650
 Ellis, 9
 Ellis, C., 544, 549, 558, 559, 565, 568, 584-586, 588, 652, 663
 Ellis, G. H., 633, 643
 Ellis, J. W., 235
 Ellis, M. M., 679, 689
 Ellis, N. R., 787
 Ellis, V. K., 429
 Ellison, T. E., 504
 Elm, A. C., 574
 Elm's, J., 575
 Elöd, E., 365
 Elsner, W., 529
 Elster, J., 97
 Elvehjem, C. A., 784, 788, 790, 836

- Emeléus, H. J., 31, 259, 317, 322, 332, 333, 358, 408, 458
 Emerson, H., 805
 Emerson, R., 869, 875, 881
 Emerson, W. B., 165
 Emmerie, A., 817, 852
 Emmett, A. D., 853
 Emschwiller, G., 246, 385, 396, 397, 399, 400
 Ende, W., 133
 Ender, F., 801, 815
 Engel, A. v., 52
 Engel, P., 756
 Engel, P. S., 849
 English, S., 169, 171
 Enos, G. M., 661
 Enotte, M., 834
 Enselme, J., 672, 766
 Enss, J., 169
 Ephraim, F., 370
 Eppley, M., 152
 Epstein, P. S., 163
 Errera, J., 412, 469
 Escalles, R., 471
 Escombe, F., 875
 Escourrou, R., 617
 Essex, H., 527, 530, 531
 Essig, B., 841
 Essinger, R., 754
 Estey, R., 366
 Estler, W., 749
 Etzler, D. H., 440
 Eucken, A., 226, 292, 293
 Euler, B. von, 792
 Euler, H. von, 432, 434, 449-451, 685-687, 689, 703, 710, 792-794, 818, 822, 849, 850, 854, 856
 Evans, E. B., 546
 Evans, H. M., 850
 Evans, J., 518
 Evans, M. G., 302, 322
 Evans, W. M., 437
 Evers, N., 855
 Everse, J. W. R., 800
 Ewald, E., 772
 Ewell, A. W., 724
 Ewest, H., 47
 Ewing, P. L., 523, 689
 Ewing, W. W., 284
 Eyber, G., 333
 Eyler, H., 670
 Eymer, J. G., 881
 Eyring, H., 288, 313
- F**
 Fabbriotti, G. F., 556
 Faber, F., 751, 755, 774, 779
 Fabisch, W., 819
 Fahre, R., 77, 523, 669, 750, 790, 795, 798, 860
 Fabrics Coördinating Research Committee, 643
 Fabrikant, V. A., 93, 119, 147
 Fabry, C., 5, 97, 107, 121, 192, 193, 195, 197, 198, 271
 Fachini, S., 555
 Färber, F., 489, 517
 Fahrion, 573
 Fairhall, L. T., 711, 754
 Failla, G., 209
 Fajans, K., 376, 378, 380, 381
 Falk, I. S., 170, 173, 196, 751
 Falkenheim, C., 779, 836
 Faltn, E., 670
 Faltings, K., 308
 Faraday, M., 6, 206
 Faraday Society, 228, 261, 262
 Fardon, J. C., 708
 Fargo, J. M., 786
 Farkas, A., 290, 337, 338, 342, 355, 394, 750
 Farkas, L., 231, 242, 259, 273, 275, 290, 301, 303, 309, 310, 317, 319, 320, 322, 337, 338, 342, 355, 402, 425, 437, 438, 451
 Farmer, E. H., 566, 574
 Farrow, F. D., 615
 Faucon, 663
 Faucon, A., 400
 Favre, P. A., 284
 Fay, A. C., 761
 Fay, H., 440
 Fazal-Ud-Din, 350, 353
 Fazel, C. S., 328
 Fazi, R. de, 432, 477, 492, 511, 517, 710, 826, 885
 Fearon, W. R., 350
 Fechner, G., 741
 Federitenko, A., 294
 Fedorov, B. T., 658
 Fedorov, F., 318
 Fedorov, F. P., 334, 465
 Feher, G., 837
 Feige, A., 74
 Feigl, F., 519
 Feist, F., 547
 Feldermann, F., 742
 Feldmann, P., 377
 Fellenberg, T. von, 777
 Fellers, R. V., 724
 Fels, E., 689
 Felsher, A., 818
 Feraud, K., 670
 Ferguson, J. B., 66
 Fergusson, W. C., 304
 Fernau, A., 390
 Fernholz, E., 689, 807, 810
 Ferrari, C. G., 723
 Ferrer, J., 408
 Ferri, C., 596
 Ferri, U., 745, 752
 Fernier, G. S., 499, 503
 Ferry, J. D., 596
 Fesefeld, H., 378
 Feussner, O., 42
 Fialkov, Y. A., 658
 Fickende, E., 601
 Fichter, F., 480
 Fiedling, G. H., 424
 Fieser, L. F., 502, 504, 809
 Fink, P., 395
 Finkelburg, W., 94, 163, 188, 236, 295, 306, 307
 Finn, A., 165
 Finzen, N. R., 734, 769
 Fischer, A., 690
 Fischer, F., 68, 69, 73, 292, 299, 819
 Fischer, H., 62, 680, 871, 872
 Fischer, W., 339
 Fiskler, F., 432
 Fischmann, C., 800, 806
 Fischmann, C. F., 819
 Fish, E. W., 824
 Fish, F., 717
 Fisher, H. L., 595
 Fisher, R., 712
 Fishgold, H., 263, 463
 Fisk, C. F., 426, 543
 Fitch, A. A., 662
 Fitch, J. S., 854
 Fitzgerald, G. F., 6
 Fix, E. L., 411
 Fizeau, A. H. L., 6
 Fjermers, E., 684
 Flanagan, G. E., 814, 839, 841, 844, 852
 Flechsig, W., 372
 Fleisch, A., 831
 Fleischhauer, R., 550
 Fleming, W. D., 782
 Fleming, W. E., 659
 Fleisch, W., 864, 879
 Flexner, L., 495
 Flinn, F. B., 825
 Florentin, D., 539
 Flores, A., 703
 Floresco, N., 611
 Florkin, M., 685
 Flory, P. J., 293, 295, 300, 325
 Flynn, O. R., 129, 638, 639
 Foa, P., 785
 Fodor, M. E., 847
 Fokeev, V. M., 661
 Folger, H. T., 716
 Follet, D. H., 853
 Fontaine, H., 124
 Fontès, G., 745
 Fonteyn, M., 458
 Fonzes-Diacon, 663
 Foote, P. D., 190
 Forbes, G. S., 43, 44, 84, 87, 88, 96, 101, 103-105, 108, 115, 119, 123, 129, 130, 182, 190, 297, 298, 330, 355, 364, 404, 418, 459, 480, 524, 536, 537, 716
 Fordyce, C. R., 621
 Forney, J. D., 47, 132
 Forsythe, W. E., 34, 110, 143, 145, 190, 194-197, 738
 Fortrat, R., 190
 Foster, R. J., 802, 811
 Foster, D. G., 624
 Foster, G. W. A., 75
 Foster, M. L., 671, 673
 Foster, P. C., 748
 Fouchault, J. B. L., 6
 Foulke, T. E., 138
 Pound, C. G., 30, 47, 132
 Fowle, F. E., 193
 Fowler, A., 25, 33
 Fowler, G. J., 346
 Fowler, R. D., 161-163
 Fowler, R. G., 64
 Fowler, R. H., 17, 377
 Fox, G. W., 308
 Fox, J. J., 249
 Fragstein, K. v., 189
 France, W. G., 567
 Francesconi, L., 559, 807
 Francis, G. V., 869
 Franck, J., 26, 34, 163, 190, 217, 229, 231, 232, 234-242, 244, 247, 257, 262, 264, 295, 302, 330, 331, 335, 337, 338, 342, 355, 357, 375, 864, 878-881
 Frank, A., 416
 Frank, I., 167
 Franke, A., 420, 473, 869
 Franke, W. K., 310, 537
 Frankfurter, W., 105, 259, 301, 302, 305, 376, 378, 464, 628, 629, 732, 739-741, 833
 Frankfurt, M., 633
 Franklin, R., 107, 128
 Franklin, R. G., 96, 382, 674
 Franta, L., 596
 Fraps, G. S., 350
 Fraps, R. M., 832
 Fraser, H. D., 79, 131, 135
 Fraunhofer, J. von, 4
 Fred, E. B., 831
 Fredenhagen, K., 380
 Frederici, 452, 482
 Freedman, P., 139
 Freeman, I. M., 156, 163
 Freeman, S., 818
 Fier, P. C., 103
 French Office Nationale des Recherches et Inventiones, 607
 French, C. S., 881
 French, H. S., 431
 Frenkel, J., 375
 Frenkel-Tissot, H. C., 751
 Frerri, M., 517
 Frerichs, M., 834
 Frerichs, R., 293
 Friesel, A. J., 4
 Freudenberg, K., 567, 670, 679
 Freund, L., 743
 Freund, M., 655, 656
 Freund, R., 823

- Freundlich, H., 389
 Freyberg, J., 493
 Frewing, J. J., 464
 Frey, C. N., 709, 822, 833
 Frey, F. E., 407, 656
 Freytag, H., 495, 498, 518-520, 646, 651, 890
 Fricke, H., 209, 402
 Fridericia, L. S., 858
 Fridlyanskaya, F. M., 571, 574
 Friedberger, E., 725, 758
 Friederich, P., 388
 Friedlander, A., 748, 774
 Friedman, I., 775
 Frieser, H., 368
 Fritsch, C., 168
 Fritsche, J., 205, 504
 Fritze, O., 142
 Fritzsche, H., 852
 Froentjes, W., 369, 464, 500
 Fröhlich, H., 373
 Fröhlich, W., 861
 From, V. C., 832, 840
 Fromageot, C., 419, 451
 Fromberg, B. M., 168
 Fromherz, H., 271, 338, 380, 663
 Fromray Co., 828
 Frontali, G., 753, 754
 Frost, F. M., 765
 Frühling, G., 131
 Fry, H. E., 885
 Fry, H. S., 361
 Fry, J. D., 599
 Fuchs, L., 801, 811
 Fust, R., 503
 Fues, E., 373
 Fugassi, P., 405
 Fujii, M., 877
 Fukukawa, F., 506
 Fujita, H., 608
 Fukumoto, Y., 161, 396, 402
 Fukushima, I., 500, 572, 625
 Fulchignoni, E., 691, 741
 Fuller, H. J., 888, 889
 Fuller, H. Q., 243
 Fulmer, E. I., 709
 Fulton, H. R., 694, 695, 711
 Fulweiler, W. H., 153, 154
 Funk, C., 780
 Funkhauser, J., 624
 Furniss, A., 747
 Fuson, R. C., 492
 Fuwa, K., 169, 172
- G**abathuler, A., 836
 Gabel, W., 550
 Gabor, D., 58
 Gabryelski, W., 432
 Gacks, H., 860
 Gaede, J., 805
 Gaedertz, A., 764
 Gaertlein, C. W., 42
 Gartner, I., 704
 Gaffron, H., 261, 264, 509, 510, 863, 864, 876, 879-881
 Gage, F. H., 271
 Gage, H. P., 165
 Galecki, A., 388
 Galeotti, G., 696
 Galinsky, A., 365
 Gallagher, P., 268
 Gallay, W., 593
 Gallerani, G., 733
 Gallois, J., 75
 Galloway, I. A., 712, 860
 Gamble, D. L., 578, 580, 585
 Ganassini, D., 449, 457
 Gandini, A., 550
 Ganguli, P. B., 391
 Ganguly, P. B., 362, 390
 Ganguly, K. L., 471, 472
 Gans, I. W., 670
 Gant, V. A., 523
 Garcia-Bauda, A., 626
- Gardano, G., 869
 Gardner, C. E., Jr., 728
 Gardner, H. A., 385, 386, 566, 569, 574, 578, 580, 581
 Gardner, J. H., 507
 Garner, T. L., 593, 600, 608
 Garner, W. E., 210
 Garot, L., 761
 Garratt, A. P., 333
 Garrett, M. W., 139, 366
 Garrett, O. F., 723
 Garrett, R. L., 860
 Garrison, A. D., 385
 Garrison, E. A., 818, 819
 Garver, H. L., 761
 Gaschler, A., 366
 Gassul, 772
 Gasteyer, T. H., 825
 Gasul, B. M., 823
 Gates, F. L., 525, 683, 696-701, 705, 706, 708, 712, 714, 755, 775, 789
 Gattefossé, H. R., 743
 Gatterer, A., 64
 Gaudechon, H., 206, 274, 281, 299, 310, 318, 322, 324, 330, 351, 359, 393, 402, 406, 408, 414, 416, 418, 422, 425, 428, 432-435, 437, 440, 448, 456-458, 461, 462, 466, 518
 Gaudenzi, A., 82
 Gault, H., 532
 Gauthier, G., 59
 Gauvain, Sir H., 770
 Gaviola, E., 251, 302
 Gaw, H. Z., 717
 Gay, E., 647
 Gebhard, K., 636, 638
 Gebhardt, K., 633
 Gedda, L., 760
 Gedyé, G. R., 319, 321
 Gee, F. H., 311
 Gee, G., 408
 Geffcken, H. H., 77, 139, 829, 840
 Gehlen, W., 837
 Gehlhoff, G., 34
 Gehrke, A., 553, 559
 Gehrts, A., 83, 93
 Geib, K. H., 290, 317
 Geigel, H., 489, 493
 Geiger, G. A., 545
 Geisel, W., 584
 Geitel, H., 97
 Gelhoff, G., 156
 Gelissen, H., 723
 Gell, P. V. W., 167
 General Development Laboratories, Inc., 184, 828
 General Electric Co., 75, 132, 142, 143, 146, 151, 169, 172
 General Electric Co., Ltd., 49, 51, 142, 150
 General Electric Vapor Lamp Co., 66, 80, 134-138, 259
 (see also Cooper-Hewitt Electric Co.)
 Genin, G., 650, 829
 Gennes, L. de, 783, 784
 Genthe, A., 567, 573
 Genthe and Co., 514
 Gentner, W., 675
 George, H., 74, 77, 131
 Gérard, M., 508
 Gerendas, M., 271
 Gericke, L., 172
 Gerke, R. H., 156, 230, 272, 275
 Gerlach, H., 360
 Gerlach, W., 42, 662, 820
 Germer, 231
 Germer, E., 131
 Germer, L. H., 11
 Gerngross, O., 167, 563
 Gersdorff, W. A., 659
- Gerstenberger, H. J., 781, 783, 837, 839
 Gerwe, E. G., 361
 Getman, F. H., 343, 362
 Getreuer, V., 702
 Gex, M., 441, 451, 651, 764
 Gheorghiu, C. V., 494, 495
 Gheorghiu, T., 467
 Ghosh, J. C., 266, 267, 361, 370, 383, 387, 418, 421, 432, 433, 440, 443, 444, 447-450, 452, 481, 484-486, 538, 540, 541, 548, 625
 Ghosh, S., 369, 387
 Giaume, C., 757
 Giauque, W. F., 217, 227
 Gibbon, P. A., 608
 Gibbs, F. B., 288, 289
 Gibbs, H. D., 103, 479, 480, 545
 Gibbs, R. C., 25, 42, 466
 Gibson, K. E., 397
 Gibson, K. S., 165, 169, 179
 Giemsa, G., 776
 Giese, A. C., 716
 Gieseler, K., 485
 Gilard, P., 168
 Gilman, H., 464
 Ginsburg, E., 336, 398
 Ginsel, L. A., 271
 Gish, G., 670
 Gish, J., 670
 Gion, L., 350
 Giordani, K., 523
 Giordano, G., 709
 Giroud, A., 849
 Girtleman, I. F., 835
 Giua, 471
 Giua, M., 485
 Givaudon, J., 656
 Givens, J. W., 670
 Giza, T., 670
 Glancy, A. E., 762
 Glaser, F., 406
 Glass, J., 754
 Glass, S. W., 52
 Glazebrook, H. H., 421
 Glazman, S., 588
 Gleu, K., 323
 Glikson, E. B., 760
 Glissman, A., 349
 Glocker, R., 209
 Glockler, G., 393
 Gloor, W. E., 589
 Glotz, G., 495
 Glysyn Corporation, 534
 Gockel, 9
 Goda, S., 479
 Godfrey, A. B., 788
 Godnew, I. N., 217, 254
 Göbel, W., 756
 Gödrich, P., 661
 Goehring, M., 621
 Göhring, R., 288
 Görne, J., 746
 Göttch, O., 821
 Goettsch, M., 85
 Götzky, S., 209
 Gohdes, W., 193
 Gohn, G., 259
 Goldberg, F., 206, 248, 524, 542
 Goldberg, I. M., 728, 748
 Goldberg, S. A., 754, 785
 Goldberger, A. von, 315, 416
 Goldblatt, H., 780, 789, 790, 804
 Goldfinger, G., 460
 Goldfinger, P., 355
 Goldheim, S. I., 445
 Goldschmidt, F., 366

- Goldschmidt, S., 511, 567
 Goldsmith, N., 479
 Goldstein, A. E., 507
 Goldstein, E., 292, 372
 Goldstein, L., 163, 236
 Goldstein, E., 75, 127, 655
 Golf, A., 838
 Gomborg, M., 626
 Gomez-Vega, P., 860
 Gonce, J. F., 775
 Gonnard, 801
 Gooch, M. E., 836
 Goodale, H. D., 755, 787
 Goodall, F. E., 829, 847
 Goode, G. P., 183, 184, 828
 Goode, C. L., 659
 Goodeve, E. F., 272, 275, 298, 306, 307, 329, 347, 395, 396, 461, 583, 857
 Gooding, C. M., 476
 Goodings, A. C., 635
 Goodman, H., 743
 Goodyear Tyre and Rubber Co., 599
 Goos, F., 178, 432
 Gorbach, G., 682, 683
 Gore, V., 869, 870
 Gordon, H. B., 640
 Gordon, J., 757, 758
 Gordon, N. E., 104, 444
 Gordon, N. T., 143, 144, 193, 195, 197, 198, 200, 385
 Gordon, R. B., 868
 Gorin, E., 439
 Gorini, F., 752
 Gorkin, Z. D., 749
 Gorony, 42
 Gorter, E., 846
 Goshorn, J. C., 385
 Goslawski, W., 479
 Gottfried, S. P., 811
 Gottlieb, K., 772
 Gottlieb, M., 517
 Goude-Axelos, J., 36
 Goudsmid, S., 25, 27
 Gough, J., 821
 Gould, A. J., 403, 422
 Gould, C. E., 167, 171
 Gourdon, G., 81
 Gouzon, B., 680, 851, 852, 871
 Gowen, J. W., 712, 836
 Goyle, D. N., 434
 Grab, W., 817
 Graef, F., 511
 Graffe, L., 608
 Graham, J. I., 329
 Graham, W. P., 762
 Gramont, A. de., 35
 Granath, L. P., 190, 193, 293, 299
 Grant, D. H., 562
 Grant, J., 169, 575, 620, 663
 Grant, J. H. B., 755, 789
 Grant, M., 366
 Grand, J., 588
 Grasse, G., 651
 Grassner, F., 464
 Grauer, R. C., 819
 Grael, O., 530
 Gray, A. E., 595
 Gray, E. Le B., 816
 Gray, E. W., 268
 Gray, G. W., 597
 Gray, L. T. M., 182, 282
 Gray, T. T., 624, 652
 Grayzel, H. G., 774, 823
 Greaves, J. E., 830
 Grechanovskii, V. P., 743
 Gredy, B., 412
 Green, D., 775
 Green, H., 597
 Green, L., 875
 Green, L. W., 652
 Greenbank, G. R., 558, 560, 561
 Greene, J., 850
 Greene, M. R., 824
 Greenfield, M., 773
 Greenwood, G., 317
 Greenwood, M., 776
 Gregersen, M., 669
 Gregory, R. A., 399
 Greinacher, H., 35
 Greider, C. E., 52, 53, 57, 115, 173, 198, 200, 841
 Griempe, P. M., 620
 Gribov, K. A., 501
 Griebel, C., 868
 Griegel, C. R., 748
 Griffith, H. D., 34, 51, 97, 800
 Griffith, I. O., 637
 Griffith, M. E., 624, 642, 643
 Griffith, R. O., 228, 281, 295, 296, 341, 351, 446
 Griffiths, J. G. A., 285, 304, 329, 431
 Grigg, P. P., 253, 288
 Grignard, V., 539
 Grimes, M. A., 616
 Grimm, H. G., 172
 Gring, J. L., 43
 Grinbaum, R., 670
 Grinstein, M., 670
 Grinten, L. van der, 105
 Groff, F., 410
 Grondall, L. O., 165
 Groot, W. de, 50, 142
 Gros, O., 206, 627
 Gross, J., 785, 822
 Grossfeld, J., 559
 Grossmann, P., 431
 Groth, W., 151, 295, 300, 308, 319, 393
 Grotrian, W., 27, 34
 Grotthuss, T. v., 205, 361
 Gruhl, A., 464
 Grumbach, A., 503
 Grumetz, M., 494
 Gün, I., 624
 Gruninger, W., 824
 Grunder, A., 581
 Grundmann, C., 425, 484
 Grundmann, W., 810, 811
 Grundy, J. G., 644
 Grunert, K., 720
 Grunfeld, M., 458
 Grünfeld, O., 598, 599
 Grüss, H., 532
 Gudden, B., 372
 Gübitz, O., 467
 Günther, E., 680
 Gunther, G., 685, 831
 Gunther, P., 9, 209
 Guntherschulze, A., 31, 82-84, 93
 Guerant, N. B., 850
 Guerrini, G., 709, 711, 861, 865
 Gucurden, J., 458
 Guha, A. C., 352
 Guha, B. C., 689, 850, 851
 Guilbert, G. D., 823
 Guillaume, 5
 Guillaume, A., 436
 Guillaume, C., 783, 784
 Guillien, R., 294
 Guillot, J., 855
 Guiteras, A., 809
 Gull, H. C., 271
 Gulland, J. M., 484
 Gunderson, F. L., 836
 Gunlikar, L. K., 882
 Gunn, F. D., 748
 Gunther, E. R., 790
 Gunther, L., 745, 754
 Gunz, A., 517
 Gupta, A. W., 267
 Gupta, D. N. Das, 485
 Gupta, P. K., 354
 Gupta, R. S., 253, 486
 Gurney, R. W., 374, 376, 379
 Gurwitsch, L., 767
 Gustavson, R. G., 813
 Gutfeld, F. V., 704
 Guthmann, H., 674
 Guthrie, E. S., 848
 Gutman, M. B., 779
 Guttman, S. A., 761
 Guyer, A., 410
 Guyot, M., 663
 Guyot, R., 479
 Guzzi, A., 504
 Gvozduer, S. D., 31, 82, 94
 Gyemant, A., 100, 105
 György, P., 754, 772, 821, 827, 850, 851
 Gyulai, Z., 372
 Haack, E., 504
 Haas, A. R. S., 872
 Haas, E., 684, 687, 688
 Haas, H. E., 255
 Haas, R., 670, 674
 de Haas, W. J., 336, 624
 Haase, E., 658
 Haase, W., 366
 Haber, F., 259, 302-304, 309, 317, 337, 338, 342, 355-357, 366
 Haber, P., 690, 759
 Haberlandt, L., 761
 Hackkowskii, V., 263
 Hackl, J., 633
 Hadden, R., 169
 Haddock, L. A., 689
 Haddfield, I. H., 614, 642
 Hadler, B. C., 531
 Haglund, E., 617
 Haendel, W., 645
 Haenny, Ch., 354
 Haerdi, W., 541
 Haessler, E. P., 796
 Haffner, F., 789
 Hagenbach, A., 47, 48
 Haggie, R., 266
 Hagne, I. M., 109
 Hahn, D. A., 518
 Hahn, G., 522
 Haig, C., 857, 859
 Haime, 691
 Haimes, R. B., 722
 Haitinger, M., 556, 663, 665
 Halban, H. von, 271, 282, 337, 351, 437, 479, 489, 493
 Halden, W., 817
 Halderson, H., 824
 Halford, J. O., 626
 Hall, B. J., 60
 Hall, G. E., 814
 Hall, H., 816
 Hall, P., 837
 Hall, R. A., 743
 Hall, R. O., 640
 Hall, V. C., 271
 Hallauer, C., 712
 Haller, R., 617, 626, 633
 Hallett, R. L., 582
 Halliday, N., 850
 Hallwachs, W., 107, 193, 269
 Halnan, F. T., 711
 Halpin, J. G., 814
 Halse, O. M., 514
 Halvorsen, H. A., 814
 Ham, A. W., 822, 824
 Hamada, H., 95
 Haman, R. W., 801, 815, 829, 840
 Hamburger, L., 85, 380
 Hamburger, T., 644
 Hamilton, C. S., 52
 Hamster, V. C., 52
 Hammarsten, E., 704
 Hammarsten, F., 704
 Hammeich, T., 684, 686
 Hammett, L. P., 495
 Hammick, D. L., 461
 Hampel, J., 506
 Hampton, W. M., 164, 167, 171
 Hanau Quarzlampen A-G., 81, 132, 176
 Händ, D. B., 685, 848

- Hand, I. F., 200
 Handley, F. W., 500
 Handovsky, H., 825
 Hanford, Z. M., 844, 852
 Hanke, M. E., 781
 Hannerz, E., 439
 Hanovia (Chemical and Manufacturing Co.), 74, 78, 80, 100, 126, 134, 135, 137, 138, 161, 844-846
 Hansen, A. M., 818
 Hansen, H. C., 777
 Hansen, H. V., 587
 Hansen, T., 775
 Hansen-Schmidt, E., 536, 548
 Hanschke, G., 530
 Hanson, E. A., 881
 Hantzsch, A., 337, 343, 352, 368, 437
 Hanyu, T., 584
 Hanzal, R. F., 823
 Hanzawa, T., 369
 Haq, M., 522
 Harada, T., 124, 366
 Harai, K., 337
 Harden, A., 311
 Harder, R., 873
 Harding, K., 139
 Hardy, M., 747, 748, 775, 776
 Hare, A., 51
 Hare, D., 887
 Haring, R. C., 365
 Harkins, W. D., 36, 366
 Harms, J., 464
 Harmsma, A., 525
 Harpuder, K., 742
 Harries, W., 68
 Harrington, E. A., 271
 Harrington, E. L., 119, 120
 Harris, D. T., 97, 116, 173, 670, 673, 678, 744, 749
 Harris, E., 617
 Harris, F. I., 670, 696, 716
 Harris, L., 105, 283, 326, 395, 401, 437, 466, 627, 628, 818
 Harris, L. J., 821, 822, 849
 Harris, M., 621, 623
 Harris, N. L., 74
 Harris, R. S., 727, 781, 835
 Harrison, 66
 Harrison, D. C., 795
 Harrison, D. N., 193
 Harrison, G. B., 377, 379
 Harrison, G. R., 87, 88, 108, 116, 119, 120, 123, 129, 130, 271, 381
 Harrison, H. A., 644
 Harrison, W., 142, 633, 635, 638
 Hart, D., 728, 729
 Hart, F. B., 784-786, 790, 836, 837, 839
 Hart, E. J., 402, 543
 Hart, L. P., 581
 Hart, M. C., 805
 Harteck, P., 151, 193, 214, 226, 259, 290, 297, 300, 303, 307-309, 317, 320, 372, 453
 Hartleb, O., 390, 437
 Hartley, G. S., 500
 Hartley, H., 474
 Hartley, J. G., 856
 Hartley, W. N., 35, 40, 193
 Hartline, H. K., 857
 Hartman, J. I., 783
 Hartmann, J., 182, 766
 Hartung, E. J., 376
 Harvey, C. E., 588
 Harvey, C. H., 513, 555
 Harvey, E. N., 876
 Hashizuma, S., 358
 Haslewood, G., 809, 816
 Hashmi, M. S., 268
 Hass, H. B., 526
 Hasse, T., 169
 Hasselbalch, K. A., 735, 736, 746
 Hassko, S., 759
 Hatanoto, T., 759
 Hatch, L. F., 526
 Hathaway, M. I., 815, 824
 Hatchesek, E., 391
 Haubold, H., 823, 824
 Hauch, J. T., 781
 Hauge, S. M., 814
 Hauptmann, H., 807
 Hauser, E. A., 601
 Hausmann, W., 188, 690, 750, 860, 861
 Hauss, H., 432
 Haussen, I., 891
 Hausser, K. W., 101, 737-739
 Hautot, A., 168
 Haverstick, E. J., 48
 Hawk, P. B., 855
 Hawkins, J. A., 210
 Hawkins, N. C., 823
 Hayashi, M., 506
 Hayashi, S., 683
 Hays, M. B., 275
 Hazen, H. H., 743
 Heath, R. F., 720
 Heathcote, R., 60
 Hebb, T., 82
 Heber, C. F., 743
 Hecht, K., 379
 Hecht, O., 408
 Hecht, S., 857, 859
 Heck, L. J., 464
 Hedges, J. J., 636
 Hedwall, I. A., 259
 Heel, A. C. S. van, 238, 370
 Heermann, P., 613, 622, 643
 Heidt, L. J., 102-104, 122, 190, 297, 298, 340, 459, 524, 670
 Heilbron, I. M., 489-491, 493, 494, 794-797, 804, 805, 809, 810, 832, 853-855, 868, 876, 882
 Heilbrunn, L. V., 716
 Heilmann, G., 818
 Heinemann, A., 415
 Heinemann, F., 827
 Heinisch, O., 885
 Heinrich, F., 333
 Heisenberg, W., 10, 26, 226, 236, 243
 Heitler, W., 163, 236, 237
 Heitz, W., 478
 Helbronner, A., 77, 78, 597, 660, 720, 721
 Helfferich, B., 680
 Helfrich, F., 331
 Heller, V. G., 848, 849
 Heller, W., 391
 Hellström, H., 630, 685, 686, 703, 856
 Helman, F. D., 791, 794
 Helmer, A. C., 847
 Hemptinne, M. de, 472
 Hemsele, 35, 40, 41
 Henderson, J. M., 754, 784, 786
 Hendrichs, W. A., 788
 Henk, H. J., 617, 624
 Henkin, H., 438
 Henne, A., 412, 663
 Henning, F., 74
 Henri, Mme., 696, 767
 Henri, V., 45, 77, 78, 153, 206, 212, 213, 241, 244, 271, 314, 326, 327, 330, 339, 394, 401-403, 412, 416, 419, 425, 431, 433, 434, 451, 458, 466, 467, 469, 521, 557, 601, 610, 660, 671, 692, 693, 696, 698, 720, 721, 737, 767
 Henrich, A., 396
 Henriques, F. C., Jr., 324
 Henriques, P. C., 629
 Henry, D. E., 98
 Henry, I., 1
 Henry, K. M., 836
 Henry, L., 160, 324
 Hensel, A., 478, 485, 490
 Henszey, R. O., 840
 Hentschel, H., 439
 Henze, M., 522
 Heraeus, 42, 68, 72, 74, 75, 151
 Herber, E. K., 890
 Herberg, E., 661
 Herber, K. W., 849
 Herbsman, A. M., 657
 Hercheinkel, H., 310
 Herck, F., 698
 Heringa, G., 754
 Hermann, N. B., 775
 Hermann, A., 244
 Hermann, P., 599
 Herms, W. B., 765
 Herold, W., 416, 425, 437, 467
 Herr, W. N., 439
 Herrie, K., 680
 Herrick, J. F., 512
 Herschberg, E. B., 504
 Herschel, J., 18, 380
 Herschel, W., 6
 Hertel, E., 248, 288, 290, 291, 400, 529, 532, 540, 697, 717
 Herter, M., 384
 Hertsriken, S. D., 172
 Hertwig, 861
 Hertz, H., 6, 26, 269
 Herwerden, M. A. van, 766
 Herzberg, G., 25, 163, 219, 228, 237, 240, 242-244, 293, 294, 326, 395, 396, 401, 414, 416, 417, 419, 458
 Herzberg, K., 712
 Herzenberg, H., 820
 Herzenstein, A., 626
 Herzfeld, K. F., 247, 276, 880
 Herzog, H., 411, 658
 Herzog, R., 617
 Hess, A. F., 773, 778-781, 783, 785, 788, 789, 791-795, 803, 813, 814, 819, 820, 822, 825, 827, 835, 836, 838, 839, 842
 Heas, J. H., 823
 Hess, K., 621
 Heas, W., 432, 434
 Hease, H., 825
 Heasler, M. C., 780
 Heasling, G. von, 464
 Heubner, W., 834
 Heudebert, 797
 Heuer, G., 757, 758
 Heurlinger, T., 220, 225
 Heuvel, F. A. van den, 566
 Hewitt Electric Co., Ltd., 179
 Hewitt, J., 624
 Heyde, V., 532
 Heyl, C., 650
 Heyl, F. W., 805, 822, 853
 Heymann, W., 819, 822
 Heymer, G., 253, 286
 Heyne, G., 64, 171, 592
 Heyroth, F. F., 698, 699, 701, 703, 850, 851
 Hibben, H. G., 98, 99
 Hibben, J. H., 224, 360
 Hibben, S. G., 142, 201, 723, 728, 729
 Ibbert, E., 508, 616, 633-635
 Hicks, 23
 Hicks, C. S., 670
 Hicks, J. F. G., 619
 Hickman, J. O., 829, 832, 841, 855
 Hickman, K. C. D., 816
 Hickman, N. V., 841
 Hickson, E. F., 579, 581
 Hida, T., 640
 Hieger, L., 804
 Higgins, G. M., 766, 788, 885
 Higgins, J. A., 523, 689
 Hilbert, G. E., 602
 Hildebrand, C. J., 823
 Hilferding, K., 279
 Hilgendorf, H. J., 322, 456

- Hilger, Adam, Ltd., 161, 270
 Hill, D. G., 400, 406
 Hill, G. A., 538, 539
 Hill, G. L., 195
 Hill, J. H., 658
 Hill, J. W., 391
 Hill, K., 680
 Hill, L., 102, 636, 640, 741, 760, 775, 776, 788
 Hill, O. J., 786, 790
 Hill, R. A., 330
 Hiller, K., 226
 Hiller, W., 384
 Hillstrom, H. T., 803
 Hülmer, A., 617
 Hilpert, S., 472
 Hilsch, R., 372, 375, 378, 379
 Himmelbauer & Co., 610
 Hinrichs, M., 717, 763-765, 767, 865
 Hinsberg, K., 553
 Hinshaw, W. R., 854
 Hinshelwood, C. N., 298, 318, 332, 422
 Hinterberger, H., 421
 Hantz, E., 650
 Hippel, A. v., 68
 Hiraoka, T., 169
 Hirsch, A., 864, 877
 Hirsch, P., 727
 Hirsch, W., 804
 Hirsch-Kauffmann, H., 785
 Hirschberg, Y., 402, 403, 425, 671, 672
 Hirschkind, W., 618
 Hirschlaff, E., 273
 Hirschlaff, E. N., 461
 Hirschler, L., 624
 Hirschhorn, H. G., 183
 Hirst, E. L., 849
 Hirst, H. R., 188, 633, 635-637, 642, 645
 Hirst, H. S., 258
 Hittorf, J. W., 36
 Hixson, O. F., 846
 Hluka, F., 519
 Hoar, S. B., 829
 Hober, H., 748
 Hoch, H., 402
 Hoch, J., 453
 Hochenbichler, A., 774
 Hochheim, E., 640
 Hodes, H. L., 822
 Hodges, F. W., 497
 Hodgson, H., 474, 479, 500, 624, 643
 Hoeber, R., 753
 Hoefelmayer, K., 841
 Hoek, C. T. van, 582
 Hoeman, E. C., 653
 Hönigsmid, O., 366
 Hörmann, H., 52
 Hövelborn, C., 741, 752
 Hoffert, W. H., 656
 Hoffman, 840
 Hoffman, J., 173
 Hoffman, La Roche, Inc., 833
 Hoffman, R. M., 122, 515, 804
 Hoffmann, A., 518
 Hoffmann, F., 35, 124, 440
 Hoffmann, J., 169, 176, 360
 Hoffmann, K., 68
 Hoffmann, R., 347, 348
 Hoffmeister, A., 676
 Hogan, A. G., 850
 Hogewind, F., 513
 Hogness, T. R., 231, 271, 456
 Hogue, J. M., 99, 738
 Hohl, J., 556
 Holborn, L., 74
 Holden, H. F., 670
 Holden, M., 712
 Holdt, P. C., 385, 386
 Hole, K. W., 59
 Holaday, E. R., 271, 670, 698, 851
 Holladay, L. L., 179, 181, 196, 583, 738
 Hollaender, A., 224, 322, 351, 707, 708, 714, 768, 776
 Holley, C. E., Jr., 572
 Holm, E., 858
 Holm, G. E., 558, 560, 561
 Holm, R., 825
 Holmes, A. D., 174, 789, 813, 834, 853, 854
 Holmes, E. O., Jr., 462, 634
 Holmes, H. H., 327, 328
 Holmes, M., 351, 358
 Holmes, W., 624
 Holmes, W. C., 443
 Holophane Co., 147
 Holst, G., 189, 630
 Holt, L. E., Jr., 784, 785
 Holtz, F., 796, 801, 821, 822
 Holtz, P., 433, 672, 673, 751, 849
 Holtzclaw, J. B., 655
 Holtzmann, 124
 Holweck, F., 8, 9, 708
 Honeywell, E. M., 792, 795, 797, 803, 813
 Hood, H. P., 169, 173
 Hood, N. R., 869
 Hooker, S. C., 502
 Hooper, C. W., 833
 Hoover, S. R., 883
 Hoover, W. H., 873
 Hopfield, J. J., 7, 272, 293, 308, 317, 325, 414
 Hopkins, F. G., 848
 Hopper, K. B., 820
 Hoppert, C. A., 790, 836, 839
 Hopwood, F. L., 556, 708
 Horclois, R., 510
 Horeish, A. J., 781, 837, 839
 Horiba, S., 389
 Horii, J., 683
 Horio, M., 467, 495, 500, 553, 558, 572, 625
 Hormuth, R., 879
 Horn, V., 786
 Horowitz-Vlasova, L. M., 560, 573
 Horton, A. T., 428, 430
 Horton, F., 156
 Hoskins, W., 765
 Hottinger, A., 792, 793, 818, 848
 Hou, H.-C., 787
 Houben, J., 339
 Houck, R. C., 679
 Houghton, E. M., 711, 726
 Houpillart, J., 509
 Householder, H., 818
 Houseman, P. A., 703
 Houtermans, F. G., 136
 Houwink, R., 584
 How, T. G., 853
 Howard, A., 489
 Howard, C. H., 175, 787
 Howard, L. B., 602
 Howard, M., 754
 Howe, H. E., 153
 Howe, J. P., 394, 428
 Howe, M. G., 754
 Howell, O. R., 314, 368
 Howell, W. H., 678, 860
 Howitt, F. O., 676
 Howland, J., 783, 784
 Hoyer, D. G., 659
 Hoyt, H. S., 670, 696, 716
 Hubert, B., 872
 Hubert, R., 755
 Hudson, D. F., 882
 Hudson, F. L., 412, 453, 454
 Hudson, H. E., 493
 Hünecke, H., 437, 674
 Hüniger, M., 169
 Huttig, G., 343
 Huetzel, F., 620
 Huffman, C. F., 790
 Hughes, A. L., 109, 269, 375
 Hughes, B., 400
 Hughes, C. W., 50, 57, 96
 Hughes, D. M., 674, 696, 716
 Hughes, J. S., 143, 787, 788, 854
 Hughes, W. A., 650
 Huish, D. M., 493
 Hukumoto, Y., 395
 Hulburt, E. O., 34, 72, 75, 106, 299, 338
 Huldshinsky, K., 778, 781
 Hulet, M., 76
 Hull, A. W., 132
 Hull, F. A., 42
 Hull, H., 814
 Hulthén, E., 237
 Hulubei, H., 95
 Hume, E. M., 779, 780, 788, 789, 792, 795, 817, 847
 Humiston, B., 317
 Hummel, C., 142
 Humphrey, G. C., 836, 837
 Hund, F., 225, 226, 228
 Hund, W. J., 656
 Hunter, A. S., 562
 Hunter, J. A., 615
 Hunter, J. E., 814, 850
 Hunter, V., 689
 Huppert, P., 172, 176
 Hurst, D. G., 161
 Husa, W. J., 657
 Hussey, R., 681, 683
 Hutchenson, A. H., 682, 711, 716
 Hutchinson, W. K., 318
 Hutton, R. S., 151
 Hyatt, C., 3
 Hyatt, J. M., 504
 Hyde, 775
 Hylan, M. C., 380
 Hylleberg, E., 236
 Ilymas, F. C., 104, 353, 400
 Ilvnek, L., 837
 Iana, I., 754
 Iancou, A., 754
 Iabak, B., 151
 Ichikawa, T., 286
 Iddings, C., 425
 I. G. Farbenindustrie, A.-G., 51, 142, 172, 176, 259, 381, 395, 411, 439, 464, 532, 534, 547, 549, 562, 621, 657, 743, 821, 832-834
 Iguchi, K., 836
 Imori, S., 106, 640
 Itholdina, C., 591
 Ikebaki, T., 742
 Ilina, Z. A., 381
 Ilina-Bagdasar'yan, Z. A., 381
 Ilina, A. A., 444
 Ilarionov, V. V., 653
 Illuminating Engineering Society, Subcommittee on Measurement of Ultraviolet Radiation, 99
 Imanishi, M., 322
 Imboden, M., 816
 Inaba, T., 573
 Inagaki, T., 165
 Indovina, R., 646, 647
 Inhoffen, H. H., 807
 Inman, G. E., 135, 141, 142, 146
 Inman, O. L., 874
 Innes, J., 821
 Inoue, T., 337
 Insko, W. M., Jr., 786
 Ionescu, A., 326
 Ionnides, Z. M., 861
 Iredale, T., 280, 306, 395, 397
 Irish, F. W., 853
 Irin, A. L., 657
 Irvine, J. C., 869
 Irving, F., 494
 Irwin, G. F., 825
 Isaac, E., 473
 Isaachsen, H., 786

- Isemura, T., 391, 436
 Ishii, S., 384, 389
 Issendorff, von, 82, 83, 84
 Issermann, S., 743
 Ito, R., 670, 685, 686, 689
 Ivanova, E. N., 444
 Iwamoto, K., 629
- Jablczynska, H., 358
 Jablczynski, K., 358
 Jack, J. M., 51
 Jackson, 66
 Jackson, A., 368
 Jackson, H., 608
 Jackson, H. C., 829, 840, 841, 845
 Jackson, W. F., 304, 309
 Jacobi, 885
 Jacobs, S., 605
 Jacobson, R. A., 411, 415
 Jacoby, D., 751, 752
 Jacoby, G., 161
 Jacqué, L., 656
 Jacquemaine, R. P., 346
 Jaquier, G., 359
 Jaekel, G., 168, 171
 Jaeger, A. O., 481
 Jaeger, C., 829
 Jaeger, F. M., 368, 438, 451
 Jaeger, M., 442
 Janicki, J., 366
 Jahn, F. P., 460
 Jais, F., 755
 Jakobson, T., 172
 Jakolewa, A., 296
 Jakowsky, J. J., 609
 Jalowy, B., 744
 James, E. M., 814, 834
 James, R. F., 723, 729
 James, T. H., 380
 Jameson, C. W., 635, 661
 Jander, G., 369, 464
 Jansen, C. H., 847
 Janssen, C., 475
 Jaubert, G. F., 293
 Jaumes, C., 747
 Jeans, Sir J., 16, 17, 191
 Jancet, P., 381
 Jancusio, F. P., 605
 Jeffreys, C. E. P., 306, 347
 Jendrassik, A., 782, 805, 809, 813, 833
 Jenkins, N. A., 325
 Jenkins, H. G., 142
 Jenkins, L. D., 586
 Jenkins, R., 637, 800, 801, 805
 Jenkins, S. S., 477, 547
 Jennen, J., 457
 Jensen, I., 562
 Jemma, G., 773
 Jephcott, H., 785
 Jerchel, D., 767
 Jermstad, A., 343
 Jessel, G., 772
 Jesserer, H., 674, 676
 Jessioneck, 769
 Jessop, G., 355
 Jessup, D. A., 621, 622
 Jette, E., 260, 262
 Jey, K.-K., 410
 Jevons, W., 227
 Jczewski, H., 163
 Jirovec, O., 523, 676, 865, 888
 Job, A., 246, 385, 396, 397
 Job, P., 343
 Jockersch, H., 274
 Joffe, C., 627
 Johanson, R., 178
 John, H., 467, 468, 518, 521
 John, C. O., 703
 Johnson, F., 784
 Johnson, F. H., 711
 Johnson, J. R., 747
 Johnson, L. B., 111-114, 135
 Johnson, M. R., 869
- Johnson, R. C., 25, 53, 228, 308
 Johnson, R. M., 818
 Johnson, T. B., 469, 518, 699, 700, 703
 Johnston, E. H., 210, 328
 Johnston, E. S., 873, 882, 887
 Johnston, H., 227, 243, 307, 325, 805
 Johnstone, F., 805
 Jokisch, R., 447
 Jolibois, P., 45
 Jolley, L. J., 458
 Jolly, J., 759
 Joly, R., 516
 Jona, A., 752
 Jonas, G. B., 149, 150, 171
 Jones, D. C. R., 506
 Jones, E. J., 327
 Jones, H. A., 659
 Jones, H. I., 586
 Jones, J. H., 785, 818, 819, 822
 Jones, L. A., 186, 271
 Jones, L. T., 397, 529
 Jones, N. C., 124
 Jones, P. F., 388
 Jones, R. N., 610
 Jones, W. J., 626
 Jones, W. N., 268, 610
 Jonsescu, A., 414
 Jonsescu, M., 472
 de Jong, A. W. K., 482, 483, 602
 Jongbloed, J., 858
 Jongh, S. E. de, 679
 Jonghe, A. de, 511
 Joos, G., 244
 Jordan, A., 743
 Jordan, D. P., 830
 Jordan, P., 163
 Jores, A., 690
 Jorg, H., 556
 Joris, G. G., 408
 Jorissen, W. P., 473, 474, 513, 514
 Joseph, C., 562
 Josephy, B., 852, 853
 Joshi, C. B., 390
 Joshi, J. N., 445, 448
 Joshi, N. V., 351
 Josse, Z., 610, 611
 Jost, W., 279, 280, 284, 542
 Juday, C., 876
 Jurgens, E., 167
 Jung, F. T., 755
 Jung, G., 246, 278, 279, 286, 371
 Jungers, J. C., 320, 407, 408, 415
 Junghagen, S., 687
 Jungjohann, W., 131
 Jusatz, H. J., 825
 Just, E. E., 764
 Justin-Mueller, E., 363, 364
- Kabanova, E. Y., 385
 Kabos, W. J., 884
 Kabat, E. A., 670
 Kachanova, E. E., 560
 Kammerer, H., 860
 Kammerling, I., 679
 Kaertkemeyer, L., 320
 Kahlenberg, O. J., 814
 Kahler, H., 97, 106, 107, 128, 194, 195
 Kailan, A., 343, 437, 440, 452, 458, 467, 480, 529
 Kaiser, H., 32
 Kakefuda, H., 851
 Kalb, W. C., 51, 62
 Kalle & Co., 481, 647, 648
 Kalish, J., 743
 Kallos-Defner, L., 752, 758
 Kallos, P., 752, 758
 Kambara, S., 593, 608
 Kambayashi, Y., 681
 Kamenskii, K. V., 885
- Kamerling, H. H., 492
 Kamerling, S. E., 878
 Kaminsky, J., 105, 627, 628, 823
 Kamm, E. D., 794, 795, 797
 Kamm, O., 792
 Kandler, L., 624
 Kaneko, H., 622
 Kangro, W., 331
 Kantzer, M., 365
 Kapella, Ltd., 165
 Kaplan, J., 163, 242, 326, 670
 Kaplan, M. Y., 588
 Kaplanskaya-Raiskaya, S. I., 742
 Kaplanskii, S. Y., 742
 Kapoor, G. P., 887
 Kappanna, A. N., 267, 442
 Kapur, P. L., 268
 Karagunis, G., 267, 380, 558
 Karel, M., 101
 Karl, P., 743
 Karlsson, S., 793
 Karpinsky, Z., 607
 Karrer, P., 849, 850, 852, 854
 Karrer, S., 328
 Karschulin, M., 362, 365
 Karshan, M., 824
 Karsten, A., 651
 Kasai, E., 172
 Kasai, K., 506
 Kasatkin, E. V., 748
 Kasheinnikova, A., 837
 Kassel, L. S., 210, 217, 316, 319
 Kassowitz, K., 775
 Kastle, J. H., 276
 Kather, E., 553, 678, 679
 Kato, N., 684
 Kato, S., 414, 416, 548
 Katowaki, H., 172
 Katschanova, E. E., 573
 Katz, E., 877
 Kauffmann, H., 613, 614, 616
 Kauffmann, H. P., 399, 457, 536, 548, 556, 565, 567
 Kaufmann, W., 172
 Kaul, L., 366
 Kautsky, H., 254, 262, 264, 265, 333, 864, 877, 879
 Kawa, J., 32, 83, 97
 Kawaguchi, S., 742
 Kawakami, K., 854
 Kawakami, T., 681, 753
 Kawasaki, K., 506
 Kayser, H. G. J., 5, 271
 Keating, 66
 Kedrovskii, B., 751
 Keenan, G. L., 383
 Keeser, E., 679, 680, 688, 710, 751
 Kehlen, H., 595
 Keilin, D., 686
 Keller, E., 491
 Keller, P., 734, 738, 760
 Kellermann, K., 216, 284
 Kellie, A. F., 848
 Kellner, B., 821
 Kellner, H. M., 271
 Kellner, L., 804
 Kelly, A., 610
 Kelly, C. B., 721
 Kelly, T. D., 727, 828
 Kelting, R. C., 92
 Kelvin, W. T., 6, 73, 78
 Kelvin Bottomley and Baird Co., Ltd., 580, 640
 Kemble, E. C., 217, 225, 227
 Keményfi, A. G., 805, 813
 Kemmler, H., 742, 825
 Kempf, R., 385, 581
 Kempner, W., 710
 Kemula, W., 393, 394, 414, 415, 501
 Kennard, D. C., 787
 Kennedy, C., 850
 Kennedy, D. J., 660
 Kennedy, T., 810

- Kenner, J., 460
 Kent, H. A., 73, 76, 77, 80, 151
 Kenty, C., 84
 Kepianka, E., 479
 Kern, J., 111
 Kern, R., 822
 Kernbaum, M., 299, 338, 339
 Kerschbaum, F., 74, 118
 Kershaw, A., 479
 Kersten, G., 841
 Kersten, H. J., 695, 887
 Kessler, 583
 Kestner, O., 102, 733, 744
 Kewley, F. E., 139
 Key, J. A., 819
 Keyes, F. G., 75, 530, 720
 Kharasch, M. S., 545, 548, 550, 817
 Khlebnikova, L. Y., 52
 Khokhlovkin, M. A., 408
 Khramova, E. F., 52
 Kidson, 193
 Kieferle, 837
 Kielwein, E., 830
 Kiepenhauer, K. O., 195
 Kiesewetter, M., 493
 Kiess, C. C., 42
 Kikuzawa, T., 817
 Killian, T. J., 81, 82, 94
 Killick, E. M., 789
 Kilpatrick, M. L., 339
 Kimball, H., 193, 200
 Kimberly, A. E., 619
 Kimmel, L., 823
 Kimovec, D., 682
 Kimura, M., 240, 273, 386
 Kimura, S., 501
 Kinele, H., 271
 King, A. A., 400
 King, A. S., 23, 26
 King, A. T., 623, 645, 679
 King, E. J., 814, 822
 King, F. A., 580, 640
 King, H., 809, 810
 King, H. S., 546
 King, P. E., 188
 King, W. N., 549
 Kinsman, S. T., 642, 643
 Kinumaki, S., 534
 Kippen, P. J., Zonen, 271
 Kipphan, H., 720
 Kirchhof, F., 593, 595, 598, 600, 604
 Kirchhoff, G. R., 4, 15, 18
 Kirchstein, B., 47
 Kirillov, E. A., 378
 Kirkbride, F. W., 416, 417, 460
 Kirrmann, A., 412
 Kirsch, W., 790, 836, 837, 840
 Kirschstein, B., 47, 49
 Kirstein, F., 725
 Kirzner, N. A., 500
 Kisch, 770
 Kisch, E., 821, 829
 Kiselev, N. M., 890
 Kiss, A., 271, 328
 Kistiakowsky, G. B., 102, 103, 158, 214, 248, 250, 282, 283, 286, 296, 298-301, 305, 306, 309, 311, 318-320, 328, 329, 336, 341, 344, 347, 414, 416, 430, 466
 Kistner, H. E., 854
 Kitagawa, K., 573
 Kitahara, S., 358
 Kitamura, S., 758
 Kitaoka, K., 640
 Kitchevatz, M., 741
 Kittel, S., 751
 Kiu, T., 198, 382
 K. L., 606
 Klason, P., 868
 Klatte, F., 410, 411
 Kläuser-Cronheim, I., 821
 Klein, A., 674
 Klein, D., 814
 Klein, G., 867, 868
 Klein, H., 531
 Klein, L., 494
 Kleiz, O., 236, 257
 Klein, R. I., 823
 Klein, S. J., 824
 Kleinau, W., 857
 Kleiner, S., 648
 Klemenc, A., 300, 394
 Klemm, A., 176
 Klemm, W., 373
 Klemme, M. S., 515
 Kler, S., 760, 765
 Kletzien, S., 790, 814
 Kletzien, S. W. F., 822
 Klever, H. W., 406
 Kline, B. E., 788
 Kline, G. M., 411
 Kline, O. L., 837
 Kling, A., 346, 539
 Klingelhöfer, W. C., Jr., 283
 Klinger, H., 474, 482
 Klingler, C., 671
 Klingstedt, F. W., 466, 469, 495, 617
 Klinkenberg, A., 651
 Klinkhardt, H., 301, 302, 305
 Klinkott, G., 349
 Klissianis, N., 684
 Klose, A., 670
 Klumb, H., 169
 Klugh, A. B., 717
 Klusmann, E., 686, 849, 854, 856
 Kluyver, A. J., 715
 Klyarfeld, B., 94
 Knandel, H. C., 814
 Knapp, A. W., 100, 103, 104, 127, 817, 831
 Knauss, C. A., 554, 567, 568
 Knebel, E., 640
 Kneer, L., 689
 Knight, B., 558
 Knipscheer, H. M., 471, 496, 499
 Kuoll, A. F., 881
 Knopf, E., 266
 Knorr, H. V., 271, 879
 Knott, J. C., 761
 Knudson, A., 781, 797, 798, 802-804, 828
 Kobayashi, C., 575
 Kobayashi, M., 368
 Kobayashi, S., 767
 Kohel, E., 82
 Kohlitz, W., 346, 401, 510
 Koboshi, S., 825
 Koch, B., 106
 Koch, E. M., 784, 813, 816
 Koch, F. C., 703, 813, 815, 816, 822
 Koch, P. P., 376
 Kocher, N. S., 592
 Kodama, S., 857
 Köhner, T., 852
 Kögel, G., 629, 632, 662, 663, 669, 680, 857, 872, 877
 Kögel, J., 475, 476
 Köhler, F., 413
 Köhler, L., 413
 Köhler, S., 620
 Köhn, M., 392
 Kölsch, R., 458
 Koenig, A., 319
 König, E., 627
 Königshäuser, J., 273
 Koenigsfeld, H., 774
 Koepke, H., 341, 750
 Koernicke, E., 95
 Koser, J., 805
 Hofman, T., 391, 756, 885
 Kogan, N. M., 625
 Kogon, M., 454
 Koh, M., 749
 Kohler, E. P., 489
 Kohler, W., 47
 Kohlrausch, K. W. F., 224
 Kohn, H., 189
 Kohn, H. I., 876, 881
 Kojima, K., 600, 611
 Kokochashvili, V., 290
 Kolbert, J. W., 129
 Koldayev, B., 756
 Kolesnikova, N. I., 445
 Kolhörster, W., 9
 Kollath, W., 669, 670
 Koller, G., 521
 Komarov, V. A., 411
 Komnick, J., 82
 Kon, S. K., 791, 802, 813, 817, 835-837, 848
 Kondo, M., 685
 Kondrat'ev, V., 231, 238, 239, 243, 254, 273, 296, 305, 309, 324, 325
 Kondrat'eva, E., 305
 Konen, H., 131
 Konovulov, F., 94
 Konstantinova-Shlezinger, M., 330, 331, 870
 Koopman, J., 747, 748, 757
 Koopmans, T., 49
 Kopaczewski, W., 691, 756
 Koper, K., 266
 Kopfermann, H., 109
 Koppelman, F., 47
 Kopsch, U., 309
 Korabel'nik, R. K., 253, 341
 Korda, P., 624
 Koratzki, W., 384
 Kornfeld, G., 137, 216, 282, 283, 330, 331, 339, 340, 443
 Kornmann, J., 756
 Korotkov, K. N., 513, 514
 Kortum, G., 161, 262, 271
 Kosbahn, T., 42
 Koschara, W., 851
 Kosche, S., 632
 Kosman, A. J., 865
 Kossovitch, N., 758
 Kostyal, L., 756
 Kotecki, A., 46
 Kothari, C. I., 468, 474
 Kouperman, A. B., 441
 Kovach, L., Jr., 64
 Kovalev, T. G., 556, 653
 Kovalevskii, I. I., 618
 Kowalsky, J. de., 41, 156
 Kozak, J., 443, 549
 Kozin, N. I., 571, 574
 Kozlov, P. V., 588
 Kozlov, V. V., 501
 Kraft, J., 370
 Krah, M., 601, 605-607
 Kral, F., 743
 Krall, S., 601, 609, 610
 Kramer, B., 783-785, 792, 805, 822, 823, 832, 835
 Kramer, M. M., 852
 Krantz, J. C., Jr., 268, 481, 658
 Krashennikov, F. N., 874
 Krasso, H., 831
 Kratinova, E. P., 837
 Kratzer, A., 220, 225
 Kraus, A., 589
 Kraus, C. A., 71, 75
 Kraus, H., 689
 Krause, A. C., 858
 Krauskopf, K. B., 289, 418, 448
 Krauss, E., 831
 Krauss, F., 343, 360, 369, 370, 444
 Krauss, W. E., 838, 841
 Krausz, G., 364
 Krauz, C., 472, 596
 Kravill, H. R., 855
 Krebs, H. A., 749
 Krefft, H., 97, 115
 Kreibich, C., 675
 Kreidl, I., 468, 507, 862
 Kreidl, Heller & Co., 508

- Kreiss, B., 376
 Kreitmair, H., 820, 821
 Kremann, R., 425
 Kremers, E., 515
 Kresling, E. K., 887
 Krestinskaya, V., 390
 Krestownikoff, A. N., 686
 Kretschmar, G. A., 46
 Kretovich, V., 868
 Kreusler, 610
 Kreusler, H., 298
 Kreveld, A. van, 271
 Kringstad, H., 555
 Krishnan, K. S., 224, 348, 352, 353
 Krishnamurti, P., 149
 Krizenecky, J., 851
 Kröger, M., 593
 Kröner, W., 124
 Kroetz, C., 753, 754
 Krogh, A., 740
 Kröllpreiffer, F., 626
 Kronenberger, A., 467
 Kronenberger, P., 679
 Kronfeld, P., 763
 Kronig, R. De L., 228, 243, 374
 Kroon, H. M., 837
 Kropa, E. L., 538, 539
 Krüger, O., 505
 Krug, R., 449
 Kruger, J. H., 780, 791
 Krumpel, O., 674, 677
 Krumpell, O., 188
 Krupski, A., 690
 Ku, Z. W., 307
 Kublitskii, A. M., 408
 Kubowitz, F., 684, 687, 710
 Kucera, C., 759
 Kudssus, H., 817
 Küch, R., 72, 84, 106, 107, 147
 Küchler, L., 475
 Kühne, H., 357
 Kukenthal, H., 343
 Kuen, F. M., 861, 862
 Kuster, W., 867
 Küstner, H., 679, 688
 Kufferath, A., 575
 Kugelmass, I. N., 790
 Kuhl, H., 410
 Kuhn, H., 95, 237, 239, 240, 249, 275, 282
 Kuhn, R., 413, 425, 685, 767, 810, 851, 852, 856
 Kuhn, W., 45, 227, 266, 318, 320, 339, 349, 350, 461
 Kuhrmann, F., 484
 Kulterén, S., 839
 Kultjugin, A., 755
 Kumanomidoh, S., 682
 Kumar, K., 874
 Kummerer, L., 474, 645
 Kunau, E., 371
 Kunerth, B. L., 852
 Kunerth, W., 201, 202
 Kunz-Krause, H., 441, 443
 Kunze, P., 136
 Kunzer, W., 332
 Kupinskaya, G. V., 346
 Kurihara, K., 849
 Kurotaki, S., 575
 Kursanov, A. L., 874
 Kurtz, H. F., 190
 Kurz, P. F., 407
 Kutzelnigg, A., 405, 589, 615, 678
 Kuz'mina, K. A., 890
 Kuz'mina, L. J., 588
 Kwincinski, L., 416, 432, 466
 Ladenburg, E., 107, 193
 Ladenburg, R., 293, 295
 Ladewig, H., 448, 480-482, 882
 Laffitte, P., 463
 Lagerberg, O., 706
 Lahousse, 801
 Lai, C., 170
 Laise, C. A., 142
 Lakshminarayanan, A. K., 503
 Lal, P., 362, 390
 Lal, R. B., 267, 698
 Laland, P., 849
 Lamar, E. S., 82
 Lamb, M. C., 650
 Lambert, J. H., 206
 Lambert, P. N., 188, 635, 642
 Lambert, R. H., 381
 Lambert, V., 673
 Lami, R., 713
 Lammert, O. M., 344
 Lampert, U., 676
 Lampitt, L. H., 559, 560, 831
 Lamplough, F. E., 169, 170
 Lambrechts, A., 479
 Lambrey, M., 157, 271, 297, 324-326
 Landau, L., 191
 Landau, M., 394, 443
 Landauer, R. S., 284
 Landelium, E., 826
 Landsberg, G., 224, 270, 317
 Landsburg, K. G., 786, 790
 Lane, C. E., Jr., 543
 Lang, R. J., 33
 Langbein, K., 47, 48
 Langedijk, S. L., 404, 476
 Langer, R., 812
 Langhe, J. E. de, 271
 Langley, S. P., 1
 Langmuir, I., 31, 47, 48, 81-84, 89, 94, 209
 Langstroth, G. O., 42
 Langton, H. M., 832
 Lantz, L. A., 635
 Laquer, F., 808, 821, 851
 Larché, K., 111
 Lardy, G. C., 430
 Larisch, J., 447
 Larsen, C. J., 832, 840
 Larsen, R. G., 489
 Larsky, A. W., 256, 832, 840
 Lasareff, P., 206
 Lasareff, W., 458
 Lasch, F., 820
 Lasse, R., 176
 Lassieur, A., 539
 Latté, W. T., 650
 Lattre, J. de, 526
 La Towsky, L. W., 51
 Lau, E., 156
 Lauebli, A., 297
 Laucini, J. I., 792
 Laudenklaus, H., 393
 Laudet, G., 49
 Laue, M. von, 7
 Lauer, G. G., 602, 603
 Lauer, K., 504
 Laun, D. D., 50
 Laurens, H., 202, 732, 733, 745-748, 754, 762, 769, 770, 774, 782, 818
 Lauman, P., 467
 Laurie, A. R., 776
 Laurin, L., 612
 Lauris, A., 305
 Lavenets, I. V., 661
 Lavín, G. I., 304, 305, 318, 683, 712
 Lavoisier, I. J., 58
 Lavrenenko, M., 593
 Lavrov, F. A., 291
 Lawrence, E. O., 157, 158
 Lawrence, J., 193
 Lazarev, P., 624
 Lazlo, H. G. de, 153, 271, 501
 Lea, C. H., 559, 560, 722
 Lea, D. E., 722
 Leadbetter, G., 76
 Lease, E. J., 883
 Leathwood, M. N., 176
 Leavenworth, C. S., 884
 Le Blanc, M., 80, 182, 209, 287, 331, 545
 Le Bon, G., 127
 Leboucher, P. J. M., 662
 Le Buzec, J., 59
 Le Bras, J., 508, 510
 Leclerc, J. A., 560
 Lecompte, J., 108
 Lederer, B., 831
 Lederer, E., 139, 853
 Lederer, E. L., 390, 437, 554
 Lederer, K., 139
 Lederle, E., 338, 339
 Lee, A. R., 788
 Lee, Wei-Yung, 849
 Leech, W. D., 853
 Leendertse, J. J., 411
 Leermakers, J. A., 405, 420, 428, 534
 Lefebvre, H., 45
 Leffmann, H., 364
 Legris, R., 450
 Leheldt, A., 483
 Lehman, A. M., 772
 Lehmann, E., 193, 295
 Lehmann, G., 746
 Lehmann, H., 178, 279, 339, 461
 Lehmann, K. B., 727
 Lehner, A., 707
 Lehner, E., 741
 Leiber, F., 632
 Leifson, S. W., 281, 293, 298, 307, 308, 325
 Leigh-Clare, J. L., 759, 790
 Leighton, P. A., 44, 84, 96, 101, 103, 115, 121, 137, 320, 321, 349, 364, 378, 393, 401, 404, 415, 419-422, 464, 475, 480, 716
 Leighton, W. G., 96, 137, 418
 Leipunskii, A., 231
 Leiser, R., 530
 Leméche, M. R., 352
 Lemoine, G., 272
 Lemmers, E., 135
 Lemon, H. B., 156, 170, 173, 196, 813
 Lenard, P., 292, 386
 Lenartowicz, J., 744
 Leudle, A., 743
 Lenher, S., 311-313
 Lennox, F. A., 60
 Lennox, F. G., 680
 Lent, E. F., 283
 Lenz, W., 225
 Lenzi, F., 754
 Leon, M., 601
 Leonard, A. G., 40
 Leonard, C. S., 853, 890
 Leoncini, G., 891
 Leopold, J. S., 825
 Leo-Werke, 847
 Lepeschkin, W. W., 750, 768
 Lepskii, S., 837
 Lepsky, S., 838
 Lerat, R., 817
 Lerch, K., 682
 Leroux, P., 373
 Lesné, E., 761, 783, 784, 819
 Lester, W. R., 176
 Lesure, A., 522, 556, 726, 756
 Leszynski, W., 380
 Lettre, 809, 810, 813
 Leulier, A., 792
 Leopold, E., 602
 Leuthardt, F., 671
 Levaditi, C., 690, 712, 824
 Levanas, L. D., 422
 Lever Bros., 847
 Leverenz, H. W., 265, 375
 Levi, H., 264, 864

- Levin, I., 852
 Levine, A. A., 534
 Levine, B. S., 758
 Levine, V. E., 752, 818
 Levinsohn, S. A., 783
 Levinson, L., 776
 Leviton, A., 447
 Levshin, V. L., 370
 Lévy, P., 566
 Lévy, S. A., 587
 Lewis, B., 272, 274, 276, 280, 286
 Lewis, G. N., 210, 294
 Lewis, J. M., 775, 785, 814, 820, 838, 839
 Lewis, M. D., 822
 Lewis, M. R., 765
 Lewis, R. C., 781, 824
 Lewis, S. J., 155, 620
 Lewis, T., 740
 Lewis, W. C., 210
 Lewis, W. C. M., 209, 347, 504
 Lewkowsitch, E., 555
 Lewschin, W. L., 262
 Lex, E., 47
 Ley, F., 271
 Ley, H., 271, 351, 425, 428, 437, 441, 458, 476, 482, 495, 671, 674
 Li, Y. P., 824
 Liberaffi, C. H., 481
 Libby, W. F., 336
 Lieben, F., 436, 449, 671-674, 676, 689, 702, 763
 Liebesny, P., 745
 Liebmann, G., 19
 Lieck, H., 849
 Lieneweg, F., 272
 Lipe, J., 457
 Lifschitz, S., 44
 Lifschitz, I., 369, 464, 479, 500, 512, 626-628
 Light, L., 479
 Light, R. F., 709, 822, 833
 Lignac, G., 740
 Lillie, R. S., 717, 764, 865
 Lillienfeld, W. E., 660
 Lima, P. de, 885
 Limaye, D. B., 478
 Limaye, P. S., 361
 Lind, S. C., 276, 278, 291, 414, 415
 Lindberg, E., 432, 449
 Lindemann, F. A., 209
 Linden, H., 860
 Linder, J., 829
 Lindner, P., 709
 Lindquist, F. E., 280
 Lindström, C. F., 396, 425
 Link, D. C., 81
 Linnett, I. W., 423, 464
 Linsert, O., 804, 807-809, 834
 Lippmann, F., 451
 Lipp, P., 515
 Lippay, F., 865
 Lippert, K. M., 860
 Lippmann, A., 744, 745
 Lishmund, R. E., 425
 Lisse, M. W., 704
 Lister, M. W., 461
 Lister, W. N., 610
 Little, C. C., 787
 Liu, T.-K., 414
 Livering, G. D., 35, 294
 Liversedge, S. G., 405
 Livings, G., 611
 Livingston, R., 259, 291, 341, 414, 415
 Ljungkvist, G., 826
 Ljungren, G., 493
 Lloyd, B., 720, 721
 Lloyd, W. V., 522
 Lobb, D. E., 815
 Locher, G. L., 101
 Lochte-Holtgreven, W., 52, 244
 Locke, F. J., 172
 Locke, F. M., 168, 172
 Lockyer, Sir N., 32, 35
 Lodati, D., 472
 Lodenkamper, H., 754
 Loeb, L. R., 40
 Loeb, M., 760
 Loeb, S., 258
 Loecker, T., 417
 Loeffel, W. J., 786
 Löhle, F., 378
 Löhner, L., 750, 860
 Loeper, M., 756
 Loew, G., 557
 Loewe, L., 436, 449
 Loewen, D. F., 823
 Lowenstein, L., 840
 Loewy, A., 761
 Loewy, A., 742, 750, 824
 Lo Grasso, H., 770, 775
 Lohaus, H., 484
 Lohfert, H., 387
 Lohmann, A., 803
 Lohse, H. W., 35
 Loiseau, G., 690
 Lojkin, M., 830
 Lombardi, L., 511
 London, F., 163, 236
 Long, B., 170, 176
 Long, F. R., 823
 Long, F. L., 874
 Long, M., 128
 Long, M. B., 97, 106, 107, 165
 Long, N. L., 818
 Long, S. H., 388
 Loofbourrow, J. R., 271, 698, 699, 701, 703, 708, 794, 804, 850, 851, 855
 Loomis, F. W., 227, 243
 Loose, L., 883
 Lord Investierungs-Korporation, A. G., 660
 Lorenz, A. J., 847
 Lorenz, E., 768
 Lorenz, H., 374
 Lorenz, L., 355
 Lorinser, P., 681
 Lotte, P., 509, 608
 Lotz, A., 366
 Louis, P., 516
 Loureiro, A. J. de, 556
 Loury, M., 510
 Louwma, H. W., 883
 Loveland, R. P., 379
 Lovern, J. A., 555
 Lovisatti, N., 740
 Lowenstein, E., 690
 Lowry, C. D., Jr., 653
 Lowry, T. M., 68, 148, 244, 355, 395, 425, 451, 515, 522
 Lubber, A., 401
 Lucas, F., 597, 714
 Lucas, N. S., 736, 739, 779, 809, 847
 Lucas, R., 450
 Luce, E. M., 781, 835
 Luce-Clausen, E. M., 773
 Luckiesh, M., 34, 46, 141, 143, 144, 147, 165, 168, 195, 583, 642, 738
 Luco Products Corporation, 172
 Lucy, F. A., 475
 Ludany, G., 689
 Ludlam, E. B., 280, 282, 283, 287, 406
 Lubeke, C., 94
 Lubeke, E., 82
 Lüers, H., 681
 Lüpno-Cramer, 367, 376, 380, 381
 Lütkenmeyer, H., 276, 278, 279
 Lüthv, A., 431
 Lüttringhaus, A., 806-808, 821
 Lumbard, V. G., 650
 Lumière Brothers, 365
 Lumière, A., 495
 Lumière, L., 495
 Lund, H., 849
 Lunt, R. W., 310
 Lundagen, M. A., 783
 Lundé, G., 555
 Lundegård, H., 35
 Lupas, I., 475
 Luszcak, A., 624, 651
 Luten-Berg, K., 565
 Luther, R., 182, 206, 214, 347, 348, 368, 504, 505, 524, 542
 Lutz, R. E., 489
 Luxat, K., 546
 Luyet, B., 707, 708
 Lyashenko, V. D., 500
 Lyman, T., 7, 21, 22, 192, 381, 698
 Lyons, E. H., 400
 Lythgoe, R. J., 857, 859
 Lyubimenko, V. N., 849, 874
 Mabbott, E. E., 546
 McAlevy, A., 517
 McAlister, E. D., 96, 108-110, 718
 Macaulay, R. M., 494
 McBaum, J. W., 588
 McBeath, E. C., 824
 McBee, F. T., 526
 Macbeth, A. K., 343, 502
 Macbeth, H. F., 657
 McBride, G. C., 862, 863
 McCaig, F., 330
 McCaskey, I., 774
 McIceland, N. P., 416, 431
 McCloskey, K. E., 567
 McCollum, E. V., 779, 835
 McConkey, C. A., 451
 McConnell, I. R., 652
 MacCormac, H., 772
 MacCorquodale, D. W., 805, 856
 McCrae, A., 890
 McCrae, H. M., 772
 McCurdy, W. H., 83
 McDonald, F. G., 792, 794, 806, 807
 MacDonald, G. D., 420
 McDonald, J. K. L., 163
 Macdonald, J. Y., 324, 325
 McDonald, R. D., 406
 Macdonald, R. F., 50
 McDonough, E. G., 423
 McElroy, K. P., 549
 McEwen, H. D., 846
 McEwen, J. L., 642
 McFarlan, R. L., 853
 McFarlane, W., 853
 McGookin, A., 489, 495
 McGowan, J. P., 818
 McGregor, T., 273
 McGroarty, W. J., 830
 McGuigan, H. A., 523, 689
 Macht, D. I., 268, 523, 658, 691, 735, 749, 865
 Machti, A., 846
 McHugh, G. P., 494
 McIlwain, H., 522
 McIntosh Electrical Corporation, 81
 Macintosh, J., 836
 Mack, E. L., 349
 Mackay, C. A., 269
 McKay, F. M., 818
 Mackay, H. M. M., 789
 McKeag, A. H., 142
 McKee, R. H., 607
 McKee, R. W., 856
 McKenna, C. B., 350
 McKenzie, H. M., 618
 Mackenzie, K. H., 782
 McKenzie, M. R., 774, 822
 MacKenzie, T. C., 400
 McKeown, A., 210, 228, 281, 296, 341, 351, 446
 McKeown, S. S., 32
 McKeown, S. S., 48, 82
 McKillop, M., 785
 McKim, W. A., 589

- McKinlay, D., 722, 831
 McKinley, E. B., 712
 MacKinney, G., 870
 McLagan, H. P., 81
 MacLean, I. S., 837
 McLean, S., 143
 McLennan, J. C., 317
 MacLeod, F. L., 837-839
 MacLeod, G. F., 718
 McMahon, P. R., 623
 McMahon, P. S., 285, 377
 McMorris, J., 371
 MacNair, W. A., 795, 813
 McNamara, T. L., 655
 McNaughton, F. E., 659
 McNicholas, H. J., 155, 165, 179, 180, 856
 McNulty, S. A., 466
 Macovski, E., 472
 McQuarrie, I., 790
 MacQuiddy, E. L., 51
 McKae, D. K., 42
 Macwalter, R. J., 368, 856
 McWillie, J., 296
 Mada, T., 354
 Maddison, R., 96, 107, 128
 Maddison, R. E. W., 255, 346, 357
 Maddock, A. J., 117, 188
 Madelung, W., 626
 Madhok, M. R., 351
 Madinaveitia, J., 502
 Maecker, H., 52
 Magaldi, F., 529
 Magee, H. E., 754, 784
 Magill, M. A., 674
 Magistri, H., 670
 Magninini, G., 328
 Magondeaux, B., 731
 Mahajan, L. D., 555
 Mahneke, H. F., 333, 413
 Maier, Fr., 562
 Maier, W., 624
 Mailey, R. D., 829
 Mainzhausen, L., 392
 Maisin, I., 511
 Majert, D., 369
 Maki, T., 624
 Makrinos, I., 754
 Malachowski, R., 456
 Malaviya, B. K., 497
 Malaviya, K. N., 538
 Malcolm, H. W., 46
 Malczynski, S., 754, 755
 Malley, R. D., 149
 Malm, C. J., 621
 Malowan, L. S., 743
 Malthy, J. G., 64
 Malus, F. L., 4
 Mamel, E., 826
 Mancho, W., 370
 Mancho, W. J., 370
 Mancini, J., 660
 Mandelbaum, J., 857
 Mandelstam, L., 224
 Mandelstam, S. L., 53
 Manecke, W., 564
 Manen, B. van, 240
 Mangini, A., 624
 Mangold, E., 745
 Mangold, P., 449, 516
 Mamcke, P., 441, 443
 Manley, J. H., 160
 Mann, M., 712
 Mannich, C., 179, 182
 Manning, W. M., 325, 428, 866, 876
 Mansfield, J. V., 548
 Manuel, S., 855
 Maquenne, 715, 887
 Marble, A., 819, 821
 March, A., 9
 Marchand, P., 651
 Marchionni, A., 741, 752
 Marchlewska, J., 388
 Marchlewski, L., 416, 431, 432, 466, 478, 479, 482, 501, 670, 688
 Marchwald, W., 268
 Marconi, G., 6
 Marcusson, J., 564
 Marden, J. W., 140, 141, 149
 Margarito, V., 611
 Marie, S. V., 630
 Marini, M., 619
 Marique, P., 862
 Markaryan, E. A., 790, 830
 Marker, R. E., 792
 Marks, H. P., 819, 821
 Marling, P. E., 572
 Marmeli, E., 710
 Marnier, L., 358
 Marras, F. M., 758
 Marriott, G. J., 506
 Marsh, J. K., 504, 511
 Marshall, A. L., 257, 258, 281, 283, 284, 287, 301, 302, 797, 802, 803
 Marshall, I. H., 816
 Marshall, S. M., 767
 Martin, A., 271, 856
 Martin, E. K., 762
 Martin, B. T., 715
 Martin, H., 227
 Martin, H. S., 167, 171
 Martin, R. B., 655
 Martin, R. C., 587
 Martin, L. C., 165
 Martin, W. H., 283
 Martinelli, A., 823
 Martinghi, G., 555
 Martini, E., 849, 852, 734, 761
 Martini, V., 761
 Martynoff, M., 478
 Marx, A., 879
 Marx, H., 774
 Marzin, A., 481
 Marzinkovskii, E. J., 776
 Masa GmbH zur Herstellung kunstlicher Oberflache, 648
 Mascarelli, I., 511
 Maschmann, E., 521
 Mashimo, T., 693
 Masland, W. E., 530
 Maslow, K., 64
 Maslow, M., 456
 Mason, D. H., 745
 Mason, F. A., 506
 Mason, H. H., 745
 Mason, R. B., 356
 Mason, R. C., 47-49, 82, 93
 Mass, E., 385
 Massaroli, P., 826
 Masseille, H., 576
 Masseneale, O. N., 787, 814-816
 Massol, G., 400
 Massol, L., 435
 Masson, M. A., 152
 Masure, M. P., 885, 889
 Matheson, M. S., 426
 Mathews, F. P., 861
 Mathews, J. H., 103, 340, 345, 356, 364, 389, 443, 497
 Mathieu, F., 819
 Matignon, C., 194
 Mathu, A. I., 631
 Mathur, K., 253, 267, 486
 Matthews, E., 283
 Matthews, F. E., 407, 548
 Matthews, F. L., Jr., 881
 Matthews, M. A., 504
 Matthias, F., 366
 Matthias, W., 84
 Mattill, H. A., 856
 Matlter, J., 101
 Matsunami, S., 405
 Matsuoka, H., 837
 Matsuoka, T., 849
 Matsuyama, F., 95
 Matushita, M., 757
 Matusis, I. I., 743
 Matzko, S. N., 837
 Mauersberger, E. A., 556
 Maughan, E., 788
 Maughan, G. H., 775, 781, 787, 788
 Mauraurour, H., 36
 Maurer, K., 679
 May, B. W., 308
 Mayer, E., 352, 706, 770-772
 Mayer, F., 549
 Mayer, G., 725
 Mayer, H., 307
 Mayer, J., 373, 432
 Mayerson, H. S., 105, 202, 733, 745-748, 754, 759, 770, 782
 Maynard, J. L., 399
 Maynard, L. A., 754, 785
 Mayneord, W. V., 556
 Mayo, F. R., 545, 548, 550
 Mayot, J., 722
 Mayrhofer, K., 259
 Maxwell, J. C., 6, 11, 16
 Mazetti, S., 368
 Mazurek, S., 610, 611
 Mazza, F. J., 460
 Mechlin, F. J., 124
 Mecke, R., 193, 208, 225, 236, 237, 240, 246, 273, 297, 299, 326, 415, 417
 Medard, L., 124
 Medlar, E. M., 754
 Meersseman, F., 823
 Meerwein, H., 852
 Mees, C. E. K., 178, 271, 381
 Meesmaecker, R., 796
 Meggers, W. F., 42, 190
 Megral, E., 690
 Megraw, H. A., 505
 Mehra, R. J., 873
 Meidinger, W., 543, 544
 Meier, F., 713, 714
 Meiler, J. G., 348
 Meissner, H., 346, 401
 Meister, G., 141, 149
 Melka, J., 745
 Mellanby, E., 795, 824
 Mellanby, M., 780, 789, 824
 Meller, B., 848
 Meller, H. B., 98, 99, 201
 Mellet, 663
 Mellor, D. P., 280
 Mellor, J. W., 282, 284-286
 Melville, H. W., 135, 182, 265, 320-322, 325, 332, 394, 415, 584, 596
 Melvin, E. H., 296
 Mencke, E., 443
 Meudel, L. B., 675
 Mendelssohn, K., 378, 379
 Mendum, W. C., 421
 Mengoli, V., 824
 Menke, I., 864
 Menschick, W., 337, 338
 Menzel, D. H., 191
 Merck (Chemische Fabrik), 832, 833
 Merck, E. Co., 837
 Merck, O., 635
 Meikel, E., 183, 743
 Merkel, H., 262
 Merory, J., 660
 Merriam, M. K., 546
 Merritt, E., 624
 Merry, J. J. F., 658
 Mersereau, G., 533
 Mertens, E., 458
 Merz, A., 871
 Merz, O., 564, 565, 590
 Mesik, R. E., 757
 Meshernistkaya, R., 750
 Mestre, H., 871
 Meunier, L., 622
 Meyer, A. v., 511, 515
 Meyer, F., 131
 Meyer, I., 683
 Meyer, J., 485, 486
 Meyer, K., 451, 553, 812

- Meyer, K. H., 596
 Meyer-Betz, F., 861
 Meyerling, D. J., 597
 Meyers, C. H., 258, 406, 563
 Meyerstein, 750
 Meyn, W., 129
 Mezener, M., 370
 Mezger, O., 663
 Mezzadrol, G., 869
 Michaud, G., 178
 Michel, J. M., 657
 Michel-Lévy, A., 36
 Michels, M., 645
 Michelson, A. A., 4, 5
 Midgley, E., 615
 Miethe, A., 97, 182, 366
 Migita, M., 477
 Mikami, H., 670
 Mikeska, L. A., 655
 Mikhailov, N. I., 612
 Mikhailovskii, S. M., 690
 Miki, T., 572
 Milanese, E., 523, 848
 Milas, N. A., 402, 405, 407, 517, 727, 832
 Milbauer, J., 264, 498
 Millam, L. H., 481
 Milten, J., 173
 Miller, C. C., 358
 Miller, E. B., 652
 Miller, E. S., 271, 854
 Müller, G. A., 822
 Miller, L. B., 151
 Miller, R. C., 754, 785
 Miller, R. D., 201, 202
 Millikan, R. A., 7, 9, 42
 Millprint Products Corp., 617, 727
 Mills, A. G., 395
 Milner, C. J., 150
 Milner, S. K., 40
 Milone, M., 461
 Mindlin, S. S., 588
 Mineral Separations N. Am. Corp., 655
 Minganti, T., 444
 Mingoia, O., 517, 726
 Minguin, J., 517
 Minkowski, R., 559
 Minor, J. E., 620
 Minor, L. C., 585
 Mironescu, E., 725
 Mirsky, A. E., 676, 858
 Mitamura, K., 836
 Mitchell, A. C. G., 92, 150, 257, 258, 319, 321
 Mitchell, C. A., 644, 663
 Mitchell, H. F., 784
 Mitchell, J. M., 836, 842
 Mitchell, J. S., 265, 676, 677
 Mitchell, J. W., 422, 889
 Mitchell, S., 515
 Mitra, B. N., 515, 670
 Mitra, M. N., 484
 Mitscherling, W. O., 657
 Mitter, B. N., 440
 Mittra, R. N., 370
 Miura, K., 434
 Miyamoto, S., 392
 Miwa, T., 684
 Miyaniishi, M., 40, 273, 301, 304
 Mizuno, K., 712
 Mizusawa, H., 686
 M. L. P., 600
 Mobley, R. L., 710
 Mochan, J., 318
 Modern, F., 691
 Möller, E. F., 809, 810
 Moelwyn Hughes, E. A., 298, 335
 Mörikofer, W., 801
 Moewus, F., 767
 Moffet, G. L., 809
 Mohammad, S. S., 869
 Mohile, B. V., 361
 Mohler, F. L., 109
 Mohr, F., 205
 Mohr, W., 839
 Mojen, H. P., 594
 Moldenhauer, O., 872
 Molinari, 471
 Molisch, H., 874
 Moll, T., 814, 821
 Moll, W. J., 96
 Mollney, E., 611
 Mollwo, E., 373
 Molnar, E., 673
 Molnar, J., 499
 Molnar, N., 728
 Molodenski, V. S., 612
 Momose, I., 586
 Monasterio, G., 865
 Moncetz, A. de., 209
 Mond, R., 675, 676
 Monden, S., 553
 Monier, J. A., Jr., 510
 Montagne, P., 45
 Montagne, R., 382
 Montfort, C., 873, 882
 Montgomery, B. E., 824
 Montgomery, C. W., 310, 315
 Montgomery, M. E., 822
 Monti, L., 474, 482
 Montignie, E., 367, 370, 812
 Monsanto Chemical Co., 481
 Monvoisin, 724
 Moody, C. A., 786
 Mooney, R. B., 406, 457
 Moor, F., 389
 Moore, A. R., 767
 Moore, B., 151, 695, 867-869, 881, 882
 Moore, C. N., 798, 804
 Moore, E. E., 688
 Moore, H. R., 109
 Moore, J. G., 887
 Moore, J. M., 787
 Moore, M. B., 688
 Moore, McF., 132
 Moore, T., 555, 791, 821, 822, 856
 Moore, W. G., 50, 59
 Morabito, F., 777
 Morales-Otero, P., 706
 Moran, W. H., 753
 Morelle, J., 819
 Morey, G. H., 447
 Morgan, A. F., 786, 818, 819, 823, 848
 Morgan, H., 188, 693
 Morgan, J. L. R., 344, 357
 Morgan, W. L., 561, 562
 Morgaredge, K., 846
 Morgen, R. A., 847
 Morgulis, S., 685
 Mori, H., 621
 Morikaw, K., 394
 Moritz, A. R., 754, 755, 790
 Moritz, H., 64
 Moriell, J. C., 652-654
 Morrell, R. S., 456, 564
 Morris, H. L., 601, 609, 610
 Morris, J. C., Jr., 269
 Morris, N., 819
 Morris, V. N., 600
 Morrison, C. G. T., 391
 Morrison, R. R., 798, 803
 Morse, D. S., 611
 Morse, M., 792, 794, 801
 Morse, P. M., 31, 236, 374
 Mortenson, R. A., 464
 Morton, D. S., 365, 524
 Morton, R. A., 97, 102-104, 129, 351, 352, 368, 431, 495, 513, 555, 794, 795, 797, 804, 853-856
 Moskalenskaya, E., 454
 Moskovich, S. M., 384
 Moss, J. E., 100, 103, 104, 127
 Moss, W. H., 585
 Mosset, M., 538, 541, 548, 549
 Mossini, A., 826
 Mott, N. F., 376, 379
 Mott, W. R., 498, 527, 640
 Mottram, J. C., 865
 Mott-Smith, H., Jr., 31, 81
 Motz, H., 376
 Moufang, E., 725
 Mougeot, P., 636
 Mougey, H. C., 586
 Mounier, D., 499, 633
 Moureaux, H., 451
 Moureu, C., 423, 509, 511, 608
 Mouriquand, G., 780, 781, 784, 792
 Moycho, V., 737
 Mrázek, S., 393, 394, 414
 Much, 691
 Mudrovic, M., 353
 Muffat, C., 478
 Mühlhausen, C., 626
 Mühlendahl, E. von, 587, 590
 Muir, J., 663
 Mukerji, B. K., 249, 252, 253, 259, 260, 337, 344, 351, 445, 446, 541
 Mukerji, D. M., 360
 Mukerji, S. K., 350
 Mukherjee, J., 433, 541
 Mukherjee, S. K., 883
 Müller, A., 424, 520, 646
 Müller, C., 464
 Müller, E., 401, 413, 439, 510, 638
 Müller, F. G., 415
 Müller, H., 283, 411
 Müller K. O., 550
 Müller, K. L., 401, 407, 535, 538
 Müller, M., 810
 Müller, R. H., 260, 262, 354, 388, 443, 449
 Müller, R. W. J., 752
 Müller-Rodloff, I., 510
 Müller-Skjold, F., 137
 Mullen, R. S., 225, 226, 228, 325, 396, 412
 Mumford, L. S., 310
 Mumm, O., 261
 Munch, R. H., 160
 Mund, W., 320
 Mündell, O., 792
 Münzinger, W. M., 591
 Munsell, H. E., 787, 814
 Muntwyler, E., 684
 Munzert, H., 564, 572
 Murakami, K., 683-685, 709
 Murakawa, K., 92
 Murarour, H., 354
 Murat, M., 423
 Murayama, M., 753, 758
 Murgulescu, I. G., 368, 442
 Murke, H., 805
 Murphy, E. F., 787
 Murphy, G. B., 653
 Murphy, G. M., 158, 159
 Murphy, R. V., 389
 Murray, G. H., 167
 Murray, J. M., 787, 836
 Murray, T. F., 591, 592
 Murthi, D. S. N., 485, 536
 Murthi, M. L. N., 486, 538
 Murty, K. S., 351, 354, 503
 Musante, C., 852
 Muskat, M., 163
 Mussehl, F. E., 814
 Myer, J. L., 46, 47
 Myers, A. E., 323
 Myers, V. C., 684
 Myrster, F. H., 179
 Myrback, K., 793
 Nubarro, D., 855
 Naeef, R., 852
 Nagai, I., 600
 Nagai, Y., 347
 Nagaoka, H., 50, 149, 366
 Nagle, P. G., 600
 Nakadate, K., 760
 Nakae, R., 825

- Nakamura, A., 368
 Nakamura, G., 95, 275
 Nakamura, H., 881
 Nakamura, K., 274
 Nakamura, M., 558, 559
 Nakamura, Y., 678
 Nakashima, M., 857
 Nakashima, T., 587
 Nakayama, A., 506
 Nakayama, Y., 690
 Nanavutty, S. H., 711
 Nandy, S. K., 418, 421
 Narasimhaswami, M. V., 268, 367
 Narayana, T. S., 273, 283
 Narayanan, B., 467
 Narayanaswamy, L. K., 348, 353
 Narayanmurti, D., 449, 481
 Nastyukova, O. K., 717
 Natelson, S., 545, 805, 811, 832
 Nath, B. V., 351
 National Carbon Co., 54-63, 173, 664, 829
 National Research Council, 96, 227, 265
 Naton, J., 493
 Naudé, S. M., 329
 Naumann, H. M., 68
 Naumann, K., 622
 Naunton, W. I. S., 599, 605
 Nauroy, A., 581, 589
 Navez, A. E., 268
 Neave, A. S., 388
 Neckel, A., 452, 482
 Negelein, E., 687, 874, 876
 Negishi, M., 587, 621
 Negresco, T., 42
 Neher, P., 357
 Neiger, R., 451
 Neilsen, C., 853
 Nekludov, V. N., 625
 Nekrasov, N. I., 874
 Nelles, M., 465
 Nelson, A. F., 536, 537
 Nelson, E. M., 793
 Nelson, H. A., 128, 556, 575, 577, 578, 580, 590
 Nelson, M., 814
 Nelson, M. T., 780
 Nelson, R. E., 531
 Neracher, O., 816
 Nerst, W., 191, 206, 212-215, 283, 284, 287, 289, 292
 Nestler, R. B., 787
 Nettmann, P., 581
 Neuber, F., 661
 Neuberg, C., 361, 431, 432, 448, 449
 Neudert, W., 518
 Neuenburg'sche Verwaltungsgesellschaft, 659
 Neuhaus, C. J., 49
 Neuhausser, A., 42
 Neuimin, H., 231, 238, 240, 241, 244, 300, 402
 Neumann, L., 537
 Neumann, W., 690
 Neuroth, H., 648
 Neuschul, P., 451
 Neuweiler, C., 339, 630
 Newwirth, R., 254, 864
 Neville, G. H. J., 298
 New, G. F., 576, 583
 Newcomber, H. S., 693
 Newell, J. M., 712, 887
 Newman, F. H., 32, 83, 163
 Newton, E. B., 679
 Newton, I., 3
 Ney, L. F., 867
 Nicholes, P. M., 354
 Nicollier, 344
 Nicholls, A. G., 767
 Nicholls, H., 832
 Nichols, A. C., 860
 Nichols, E. F., 6, 183
 Nichols, E. L., 19, 265
 Nichols, J. B., 181
 Nickelsen, O., 740
 Nicol, J., 48
 Nicola, O., 809
 Nicolaysen, R., 818
 Nicolet, B. H., 447, 541
 Nicolet, G., 343, 344, 485, 488
 Nicolie, D., 353
 Nicolson, D. G., 572
 Nicolson, M. G., 140
 Niederhauser, 636
 Niederhoff, P., 431, 451
 Niekerk, J. van, 800, 811, 815
 Nielson, H., 830
 Nies, N. P., 400, 536
 Nigudkar, K. D., 361
 Nimmya, H., 643
 Nijveld, W. J., 853
 Nikiforov, A. Y., 82
 Nikiforov, V. K., 392, 408
 Nikitine, S., 383
 Nikolai, F., 171
 Ninomiya, R., 758
 Nishet, J., 81
 Nishioeda, M., 877
 Nishizawa, Y., 385, 589
 Nitchie, C. C., 64, 175
 Nitschke, A., 826
 Nitta, B., 865
 Nitzeacu, I. I., 727, 793, 819, 822
 Noack, K., 261, 498, 862
 Noddack, W., 209, 211, 215, 377, 381, 532
 Noel, L. von, 846
 Nogemi, Y., 706
 Nogier, T., 127, 720
 Nolf, L. O., 718
 Noll, A., 620
 Nomura, R., 831
 Nonaka, M., 564
 Nonidez, J. F., 755
 Nordenson, H., 387, 388
 Norris, E. R., 855
 Norris, R. J., 708, 726, 828, 855
 Norrish, R. G. W., 247, 248, 258, 285-287, 289, 290, 298, 302-304, 326-329, 406, 416, 417, 419-422, 425-427, 429-431, 457, 460, 461, 524
 Northrop, J. H., 683
 Northrup, E. F., 48
 Norton, A., 261
 Norton, B. M., 397, 398
 Norton, J. F., 704, 720
 Notevert, O., 853
 Nothaas, R., 745
 Nottingham, W. B., 46-48
 Novacek, E., 556
 Novak, F. J., 776
 Novikov, V. A., 890
 Novotny, C. K., 597
 Noyes, W. A., Jr., 214, 228, 236, 294, 295, 302, 318, 319, 324, 325, 333, 348, 413, 417, 425, 426, 428, 429, 439, 441, 447, 543
 Noyons, A., 764, 858
 Nozicka, F., 468, 507, 862
 Nurnberger, C., 629
 Nussbaumer, T., 560
 Nussmeier, M., 806, 814
 Nutting, P. G., 74
 N. V., Chemische Fabrik L. van der Grinten, 105
 N. V. Elektrochemische Industrie, 360
 N. V. Philips Gloeilampenfabrieken, 77, 139, 141, 142, 149, 150, 156, 171, 172, 479, 646, 648, 829, 833, 834
 Oatway, W. H., 823
 Oberhauser, F., 445
 Oberth, S., 601
 Obrenov, I. V., 336, 501, 504, 624
 O'Brien, B., 57, 193, 832, 846
 O'Bryan, H. M., 617
 Oda, R., 504
 Oday, A. B., 144, 147
 Oddo, G., 646, 647
 Oertel, W., 348
 Oettingen, W. F. v., 734, 751
 Offant, C., 761
 Ogawa, M., 751
 Ogawa, W., 584
 Ogg, R. A., Jr., 44, 320, 321, 349, 486, 546
 Oguri, S., 111, 619
 Ohl, F., 619
 Ohle, H., 851
 Ohlsen, H., 434
 Ohlsson, E., 743
 Ohmori, M., 625
 Okamura, T., 685
 Okii, I., 817
 Okinaka, T., 530
 Okubo, J., 95
 Okuyama, K., 607
 Olcott, H. S., 856
 Olcovich, H. S., 856
 Oldenberg, O., 163, 181, 182
 Olivier, J., 756
 Olivier, S. C. J., 546
 Olson, A. R., 258, 318, 406, 412, 413, 445, 453, 454
 Olson, T. M., 786, 835
 Olsson, E., 244
 Omar, W., 758
 Omori, M., 500
 Onoda, T., 311, 314
 Onslow, G. A., 671
 Ontario Research Foundation, 640
 Oosterhuis, F., 146
 Opisso, F., 807
 Oppenheim, E., 831
 Oppenheimer, F., 151
 Orehkova, T. A., 885
 Orslup, J. W., 743
 Orlov, S., 776
 Orlova, O. V., 587
 Orndorff, W. R., 466, 504, 505
 Orne, S. W., 51, 57
 OrNSTEIN, L. S., 48, 49, 52, 97, 210, 271
 OrNSTEIN, T., 755
 Orr, A. P., 767
 Orr, J. B., 754, 784, 786
 Orr, W. J., 784, 785
 Ort, J. M., 673
 Orth, O. S., 402
 Orton, K. J. P., 497
 Os, D. van, 513
 "Osa" participations industrielles, 169
 Osborn, T. W. B., 103, 757
 Oschchipkov, F. P., 168
 Oser, B. L., 835
 Oshima, G., 684
 Oshima, Z., 677
 Osipov, A. P., 890
 Osram Co., 156
 Ossenbrüggen, W., 293
 Østby, O., 343
 Oster, R. H., 707-709
 Osterhout, W. J. V., 872
 Ostrikov, M. S., 870
 Ostrimuislenski, I., 409, 597
 Ostwald, W., 876
 Osugi, S., 350
 Ott, H., 550
 Ottensooser, F., 690
 Ottmer, R., 372
 Otto, B., 413
 Otto, H., 851
 Otto, M. P., 720

- Ouellet, C., 439, 443
 Owen, E. A., 115
 Owen, J. R., 812
 Owens, W. L., 710
 Owens, J. S., 64, 662
 Oxford, A. P., 549
 Oxholt-Howe, H., 441, 444
 Oya, T., 681
- P**
 Pabst, E., 583
 Pace, J., 684
 Pace, N., 860
 Pachioli, R., 824
 Pacini, A. J., 617, 660, 828, 834
 Packard, C., 732
 Padelt, E., 297, 307
 Padgett, F. W., 531
 Padmanabhan, R., 426
 Padoa, M., 250, 254, 255, 291, 441, 443, 444, 485
 Padovani, C., 529
 Page, I. H., 822
 Page, L., 227
 Pagel, H. A., 345
 Paget, R., 147, 151
 Paic, M., 690, 759
 Paillard, H., 62, 533
 Paine, C., 624
 Paint and Varnish Research Lab., Berlin, 592
 Pakschwer, A., 632
 Pakshver, A., 615
 Pal, N. L., 882
 Palit, C. C., 432, 450, 553
 Pallasko, G., 792
 Pallu, R., 354
 Palm, T. A., 778
 Palmer, F., Jr., 208, 349
 Palmer, L. S., 850
 Palmiero, G. G., 709
 Panchenkoy, G., 602, 653
 Pandalai, K. M., 458
 Papcke, G., 742
 Papp, S., 782
 Pappenheimer, A. M., 779-781, 783, 856
 Pardee, K., 772
 Parisi, M., 75
 Park, E. A., 779, 780
 Parke Davis & Co., 659
 Parker, A. F., 330
 Parker, H. O., 653
 Parkin, J., 868
 Parkinson, N. F., 720
 Parks, H. C., 566, 569, 578
 Parsons, W. B., 1, 2
 Parti, Y. P., 240, 395, 396
 Pascal, P., 451
 Paschen, 20, 22
 Patat, F., 292, 300, 394, 402, 417, 420, 459, 475
 Patek, A. J., Jr., 857
 Patel, C. K., 616
 Patent-Treuhand Gesellschaft für elektrische Glühlampen, 49, 137, 142, 150, 832
 Paternò, E., 477, 533
 Patitz, G. J., 709
 Paton, R. F., 26
 Patrick, W. A., 462
 Patry, M., 463
 Patten, C. G., 176, 358
 Patterson, M. L., 60
 Pattison, C. L., 824
 Patton, I. J., 216
 Patton, J. W., 777
 Paul, B., 398
 Pauli, W. E., 735, 737
 Pauli, W., Jr., 25
 Pauling, L., 378, 676
 Pauthenier, 59
 Pauthenier, M., 354, 463
 Pavlik, M., 472
 Pavolini, T., 363, 384, 450
- Pawlikowski, J., 83
 Payne, L. F., 787, 788
 Payte, J. I., 751
 Pazdor, F., 549
 Peachy, S. J., 601
 Peacock, P. R., 803, 854
 Peacocke, T. A., 404
 Peake, J. S., 64
 Peakin, F. H., 494
 Pearce, G. W., 890
 Pearvall, W. H., 883
 Pearson, A. M., 659
 Pearson, T. G., 421, 429
 Pech, J. L., 255
 Peczkalski, T., 57
 Peden, O. D., 819
 Pedrini, F., 476
 Peck, A., 679
 Peemöller, F., 691, 733, 744
 Peierls, R., 372, 375
 Peklo, J., 876
 Pelletier, M., 451
 Pelizzola, C., 605
 Pelton, M. O., 190
 Pennetti, G., 688
 Penney, W. G., 374
 Percival, W. C., 889
 Perdrau, J. R., 860
 Perlman, T., 291
 Perino, J., 722, 828
 Perkin, A. G., 506
 Perkin, F. M., 66, 74, 76, 720
 Perkin, W. H., 488
 Perkin, W. H., Jr., 547
 Perkins, R. G., 720, 725
 Perot, A., 5, 84, 273
 Perret, A., 371
 Perrin, F., 261
 Perrin, J., 209, 262, 631
 Perrot, R., 470
 Perty, J. W., 190
 Peskind, S., 773
 Peskov, N. P., 179, 181, 182
 Pestalozzi, S., 635, 644
 Pestemer, M., 271, 337, 425, 467, 504
 Peters, K., 537
 Peters, R. A., 851
 Petersen, W. F., 734, 751
 Peterson, A., 624
 Peterson, W. H., 831
 Peter, C. K., 772
 Petterson, A., 759
 Petterson, F., 760
 Pettit, E., 198
 Petri, W., 660
 Pettie, G. F., 776
 Petrikala, A., 358
 Pfahler, K., 852
 Pfannstiehl, W., 823
 Pfannenstiel, W., 825
 Pfeiffer, I., 530
 Pfeiffer, J. P., 661
 Pfeilsticker, K., 507, 876
 Pferdemenes, H., 832
 Pfister, M., 671
 Pfüger, 106, 107
 Pfunder, N., 611
 Pfund, A. H., 49, 372, 385, 386, 576, 582
 "Pharmagans" Farm. Ins., 670
 Phelps, D. V., 171
 Phelps, W. M., 770, 772, 773
 Philbert, A., 860, 861
 Philip, G., 81
 Philippe, M., 690
 Philips Lamp Co. (see N. V. Philips Gloeilampenfabrieken)
 Philipsky, A. J. H., 660
 Philips Petroleum Co., 656
 Phillips, J. B., 853, 854
 Phillips, N. W. F., 127, 394
 Phillips, R. A., 825
 Philpot, J., 806, 821, 851
 Phipps, T. E., 373
- Physical Chemistry Research Co., 652
 Piasecka-Zeyland, E., 823
 Piatti, L., 127
 Piaux, L., 412
 Piccini, C., 496
 Pichler, F., 890
 Pick, H., 682
 Pickering, 33
 Pickett, I. W., 209, 413
 Pictet, A., 435
 Pienkowski, S., 95
 Pierce, E. W., 638, 643
 Pierce, G. W., 77
 Pierce, R. F., 66
 Pierce, W. C., 443, 447
 Pierucci, M., 59
 Piggott, M. G., 174, 789, 834, 854
 Pilar, F., 766
 Pilkington Bros., Ltd., 170, 171
 Pillemmer, L., 684
 Pincus, G., 124
 Pincussen, L., 680-687, 703, 704, 745, 746, 751-756, 760, 830, 857
 Pines, C. C., 364
 Pink, H. R., 647
 Pinoncelli, L., 559
 Pinte, J., 635
 Piper, J., 624
 Pirani, M., 40, 47, 49, 115, 136
 Pirie, N. W., 712
 Pirrone, F., 432, 517, 710, 826
 Pischke, K., 868
 Pisauzhevskii, I. V., 253, 341
 Pischulna, A. F., 625
 Pittenger, P. S., 658
 Pittsburgh Plate Glass Co., 167
 Pitzer, E. G., 104, 444
 Pitha, A., 366, 460, 516
 Pizio, J., 431
 Planck, M., 10, 17, 21,
 Platt, S. S., 742
 Platz, H., 385
 Plauson, H., 411, 584
 Plaut, F., 849
 Plaut, R., 744
 Plisov, A. K., 496
 Plukhotzki, E., 94
 Plotnikow, J., 64, 205, 248, 255, 256, 292, 299, 305, 343, 360, 362, 364, 365, 377, 404, 409, 469, 522, 540, 634
 Poddulyny, W., 375
 Podrouzek, R. N. V., 124
 Poelt, H., 837
 Poggi, R., 517
 Pohle, H., 597
 Pohl, R. W., 265, 372, 375, 378, 379, 795, 797-799, 808
 Poincaré, J. H., 17
 Poindexter, F. E., 378
 Pokhil, A. I., 837
 Polak, I., 243, 273
 Polanyi, M., 265, 276
 Polden, D. C., 649
 Polcard, A., 824
 Polm, V., 31
 Pollaczek, K. F., 675
 Pollitzer, E., 416, 420
 Pollock, B. F., 747
 Pollok, J. H., 40
 Poncher, H. G., 823
 Ponomarev, F. G., 494
 Ponte, M., 95
 Pontus, P., 679
 Poole, H. H., 103, 108, 872
 Popescu, C., 631
 Popoff, M., 660
 Popov, B., 258, 300, 309
 Popoviciu, G., 793, 819, 822
 Popovitzki, A., 365
 Popp, H. W., 885-887, 889
 Porcher, C., 670
 Poremski, V., 188

- Porret, D., 275, 370, 396, 404, 480, 487, 872
 Porritt, B. D., 593, 599, 610
 Porter, C. W., 425, 431, 437, 439, 478, 497, 869
 Porter, J. M., 307
 Porter, L. C., 144, 147
 Porter-Levin, T., 830
 Portheim, L., 873
 Pospelov, A., 179, 390
 Pospelova, K., 390
 Post, C. I., 838
 Postovskii, I. Y., 512
 Potencier, R., 722
 Potopenko, G., 42, 178, 182
 Potter, 773
 Potter, H. N., 293
 Potterill, R. H., 360
 Potthoff, P., 757
 Potts, J. C., 287, 289
 Pougnet, J., 367, 487
 Poulter, T. C., 487
 Povenz, F., 396, 425
 Powers, G. F., 779, 780
 Pozzi, L., 822
 Pozzi, M., 672
 Prachel, C. U., 588
 Prager, M., 670
 Prakash, O., 447
 Prasad, M., 360, 361
 Pratesi, P., 518
 Prather, E. O., 814
 Pratt, D. S., 479, 480
 Pratt, F. L., 695
 Pratt, M. C., 868
 Pratt, R., 882
 Praudière, E. de la, 428, 430, 477
 Predwoditeff, A., 317
 Pieiss, K., 620
 Preiss, S., 646
 Prescher, W., 860
 Presnell, A. K., 826
 Presslicht-Patent-Verwertungsgesellschaft, 60
 Preto, E., 822
 Preuss, L. M., 831
 Preusze, K. H., 599
 Pribram, R., 869
 Price, W. A., 195, 786, 787, 831
 Price, W. C., 396, 414, 416, 437, 467, 712
 Price, T. S., 379
 Pridoux, F., 624
 Priest, G. W., 650
 Priest, W. J., 546
 Priestley, J. H., 868
 Prigent, G., 318
 Priik, E. M., 541
 Prikhofko, A., 294, 501, 504
 Prileshaeva, N., 464
 Pringsheim, E., 285
 Pringsheim, P., 261, 262, 264, 273, 443, 467, 665
 Priou, R., 508
 Pritchett, I. W., 825
 Privault, M., 262
 Probst, O., 490
 Proft, H., 741
 Proks, J., 695
 Prosser, 66
 Prouty, W. O., 141
 Pruckner, F., 475, 849
 Pucher, G. W., 884
 Puchkovskii, B. S., 625
 Püringer, K., 862
 Pukall, W., 485, 486
 Pulewka, P., 789
 Pulkhi, I. H., 709
 Pulman, A. O., 650
 Pummerei, R., 593-595
 Putcell, R. H., 358, 421, 429
 Purkayastha, R. M., 253, 267, 362, 448, 450, 486, 540, 548
 Purkis, C. H., 460, 461
 Purvis, J. E., 416, 431, 476, 479, 482
 Pusch, L., 211, 276
 Putland, A. W., 557
 Putschar, W., 821
 Puxeddu, E., 361, 367
 Puzenkin, E. S., 104, 452
 Puzitschki, K. W., 653
 Pye, D. J., 618
 Pyhala, E., 651
 Pyle, S. I., 789

Q
 Quaker Oats Co., 829
 Quartz Fondu, 151
 Quartz et Silice, 151
 Quarzlampen-Gesellschaft, Hanau, 132, 725, 832
 Quilico, A., 513
 Quin, J. I., 860, 861
 Quinlan, F., 385
 Quinn, E. J., 853, 856
 Quinquad, A., 754
 Quint, F., 647
 Qureshi, M., 340, 341, 428, 869
 Qvist, W., 550

R
 Raab, 860
 Rabate, J., 432
 Rabinovich, A. J., 381
 Rabinowitsch, E., 228, 232, 233, 235, 242, 244, 273, 279, 335, 336, 345, 544, 872
 Rabinowitz, L., 585
 Raczynski, J., 778
 Radley, J. A., 624, 645, 663
 Radulescu, D., 460, 467
 Radulescu, G., 654
 Ragaz, Y., 533
 Ragg, M., 586
 Ragins, I. K., 813
 Rahman, M. K., 340
 Rahn, O., 696, 708
 Rajewsky, B., 675
 Rajvansi, A. R., 870
 Rakestraw, N. W., 322
 Rakshut, P. C., 432
 Raleigh, J. T., 630
 Ram, A., 194, 367, 860, 867, 869, 870
 Raman, C. V., 224
 Ramart-Lucas, Mme., 399, 412, 432, 453, 458, 467, 482, 494, 495
 Raup, D. G., 816
 Ramsauer, C., 387
 Ramsbottom, J. E., 69, 292, 293, 307
 Ramsey, G. B., 711
 Ramperger, H. C., 431, 437, 439, 459, 478, 499, 869
 Ramstetter, H., 173, 584
 Ranc, A., 402, 403, 433, 434
 Randall, J. T., 142
 Random, L., 849
 Rangcharya, T. L. K., 444
 Ransford, R. B., 544
 Rao, A. L. S., 364
 Rao, B., 367
 Rao, E. I., 268, 367
 Rao, G. G., 193, 210, 247, 259, 350, 354, 458, 673, 869, 870
 Rao, P. S., 503
 Rao, R. H. R., 488
 Rao, S. V., 358, 367
 Rapieff, 66
 Rapoport, M., 822
 Rappaport, B. Z., 823, 824
 Rascio, R., 770
 Rasquin, H., 556
 Rassweiler, G. M., 26, 663
 Rast, K., 489
 Rathemacher, C. P., 531
 Rathenau, G., 298, 359, 382
 Rathier, J., 662
 Rathke, B., 463
 Rathmann, F. H., 853
 Ratsimamanga, R., 849
 Rau, F., 489
 Rauch, A., 624
 Rauch, H., 796, 797
 Ravault, P., 824
 Ravensway, H. J., 564
 Ravitz, S. F., 344, 363, 446
 Rawling, S. O., 379
 Rawlins, F., 239, 360
 Ray, B. B., 450, 452
 Ray, J. N., 522
 Rayleigh, Lord, 16, 36, 48, 95, 193, 268, 592
 Read, B. E., 849
 Read, J. W., 723, 830
 Rebière, G., 798, 804
 Rebmann, A., 869
 Recklinghausen, M. von, 73, 77, 78, 660, 720, 721
 Recsey, E. v., 81, 829
 Recsey, N. V., 81, 829
 Redd, W. R., 727
 Reddie, J. W., 853
 Redman, R., 888
 Reed, C. I., 703, 733, 735, 736, 746, 751, 753, 754, 785, 819, 822, 824, 826
 Reed, M. C., 612
 Reerink, E. H., 115, 142, 799, 801, 803, 805-808, 815, 829, 833
 Reeve, L., 96, 107, 128, 246, 439, 441
 Regener, E., 9, 292, 318
 Rekenner, V. D., 193
 Reggiani, M., 869
 Regulski, H., 64
 Rehman, R. A., 396
 Rehren, I., 257, 302
 Reich, V., 556, 665
 Reichel, L., 511
 Reichel, S. von, 810
 Reichert, B., 743
 Reichstein, T., 816
 Reid, E. W., 579
 Reid, H. G., 457
 Reiff, O. M., 656
 Reihlen, H., 124, 464
 Reimann, A. L., 131
 Reimer, M., 484, 491, 492
 Rein, H., 635, 638
 Reinartz, F., 515
 Reindel, F., 796, 797
 Reinders, W., 380
 Reinemund, K., 852
 Reiner-Deutsch, W., 728
 Reinhard, M., 479, 803
 Reincke, H., 414
 Reimers, J. H., 57
 Reissaus, G. C., 359
 Reiter, T., 57, 58, 821, 828, 829
 Reith, F., 765
 Reithmüller, C., 101
 Rekling, E., 782
 Reman, G. H., 877
 Remennikova, V. S., 588
 Remezov, I., 794
 Remotti, E., 765
 Rendell, L. P., 624
 Renner, F., 507
 Reinhard, A. W., 710
 Renosto, G., 761
 Rentschler, H. C., 97, 98, 141, 729
 Renz, C., 350, 360
 Repony, D., 610
 Research Association of British Rubber and Tyre Manufacturers, 610
 Retschinsky, T., 31, 72, 82, 84, 106, 107, 366
 Retter K., 447

- Rey, G., 622
 Reychler, A., 344, 629
 Reyher, P., 793, 820, 848
 Reyn, A., 769, 770
 Reynaud, 663
 Reynolds, E. S., 688, 710, 889
 Reynolds, F., 139
 Rezzesi, F. D., 862
 Rhinhold, J. S., 755
 Rhodes, G. H., 616
 Ribaud, G., 249
 Ricard, R., 382
 Rice, F. O., 210, 214, 303, 327, 339
 Rice, G. P., 491
 Rice, J., 210
 Rice, O. K., 243
 Richardson, A., 282, 376
 Richardson, E., 592
 Richardson, L. R., 850
 Richardson, O. W., 156
 Richardson, R. S., 192
 Richter, C. M., 659, 828
 Richter, G. A., 619
 Richter, H., 77, 139, 829, 840
 Richter, O., 873
 Richter, V., 839
 Rideal, E. K., 210, 258, 265, 274, 276, 280, 287, 319, 321, 329, 344, 542, 676
 Rider, T., 828
 Riding, R. W., 271, 351, 352
 Ridyard, H. N., 108, 190
 Rieche, A., 339
 Ried, O., 556, 563, 662, 728, 828, 831, 840
 Riederer, H. S., 526
 Rienzo, A. de, 819
 Riesenfeld, E., 366
 Riesenfeld, E. H., 408, 644
 Rigby, R., 60, 661
 Riggert, K., 505
 Right, R. E. De, 399, 537
 Rising, B. M., 831
 Rimington, C., 623, 861
 Rimpel, H., 599
 Ringer, W. E., 473
 Rinse, J., 575
 Rinskaja, E. S., 341
 Ris, H., 635
 Risak, E., 740
 Risler, J., 183, 583, 743, 860, 861
 Risse, O., 209
 Ritchie, K. S., 360
 Ritchie, M., 279, 283, 289, 290, 297, 300
 Ritschl, R., 26
 Ritson, K., 715, 885
 Ritter, G., 376
 Ritter, E., 580
 Ritter, J. J., 491
 Ritter, W., 560, 562
 Ritzenhaler, B., 429
 Rivat, G., 539
 Rivers, T. M., 712, 775
 Rivière, C., 463
 Rivkin, H., 785, 814
 Roach, F., 64
 Roadhouse, C. L., 835
 Robert, E., 438, 455
 Roberts, R. E., 814
 Robertson, D. F., 825
 Robertson, E. B., 849
 Robertson, E. C., 775, 825
 Robertson, H., 642
 Robertson, J. D., 785
 Robertson, R. M., 48
 Robin, 724
 Robinet, P., 516
 Robinson, F. W., 60, 103, 832, 840
 Robinson, H. A., 42
 Robinson, R., 506
 Robison, R., 818
 Robl, R., 105
 Robson, G. M., 822
 Robuschi, L., 860
 Rocard, Y. A., 59
 Roche e Silva, M., 863
 Roche, H. J., 785
 Roche, J., 670
 Roches, C., 384
 Rochette, J., 742
 Rock, E. N., 860
 Rodebush, W. H., 217, 283, 530
 Rodionov, S., 101
 Rodloff, G., 352
 Rodriguez-Ely, 720
 Rodwell, R. V., 165
 Roe, E., 809
 Roehm and Haas Co., 584
 Röhm, O., 584
 Römer, R., 337
 Röntgen, W. K. von, 7
 Rössler, F., 97, 111
 Rossler, G., 337
 Roets, G. C. S., 861
 Roffo, A. E., Jr., 742
 Roffo, A. H., 669, 742, 766, 803, 815, 872
 Rogai, F., 891
 Rogers, A. O., 531
 Roginskii, S., 318
 Rogoski, W., 40
 Rogovin, Z. A., 588
 Rohde, H. W., 722
 Rohr, F., 840
 Rohr, H., 680
 Rohrbach, E., 565
 Rojahn, C. A., 658
 Rokhlun, G., 119
 Rollefson, G. K., 214, 237, 244, 272, 280, 287-290, 298, 310, 312, 313, 315, 336, 418, 425, 440, 448, 532, 537, 539
 Rollett, A., 410
 Rollier, A., 770, 772-774
 Rollwagen, W., 49
 Rolph, F. W., 147
 Roman, L. H., 418, 870
 Roman, W., 687, 760
 Romanova, K., 523, 776, 865
 Romeyn, H., Jr., 333
 Rompe, R., 47, 49, 83, 94
 Roncallo, L., 733, 734
 Rondani, P., 790
 Roof, J. G., 420, 424
 Rooksby, H. P., 131
 Root, R. W., 752
 Rosanova, V., 853
 Rosario, U. del, 713
 Roscoe, 205, 206, 271
 Roscoe, H., 285
 Roscoe, M. H., 789, 836
 Rose, C. H., 572
 Rose, G., 171
 Rose, M. von, 754
 Rosebury, T., 824
 Rosen, B., 273, 576
 Rosenbach, J., 549
 Rosenberg, W., 624
 Rosenblatt, M. B., 824
 Rosenblum, C., 414, 427
 Rosenbohm, E., 479
 Rosenfeld, P., 862
 Rosenheim, A. H., 818
 Rosenheim, O., 788, 789, 791, 792, 794-798, 804, 809, 810, 822, 853
 Rosenmund, K. W., 546
 Rosenstein, I., 656
 Rosenthal, I., 589, 612
 Rosenthal, J., 853
 Roseveare, W. E., 445
 Roskin, G., 523, 776, 865
 Rosney, W. C., 431
 Ross, J. C., 829
 Ross, J. R., 775, 825
 Ross, W., 38, 343, 361, 430
 Rossceland, S., 193, 257
 Rossem, A. van, 603
 Rossi, A., 819
 Rossi, G., 362, 629
 Rossini, F. D., 241
 Rossmann, E., 565, 566
 Rosssner, E., 674
 Rost, G. A., 734, 769
 Roth, E., 861
 Röth, L. E., 868
 Rothmann, A., 746
 Rothmann, H., 734, 751
 Rothmann, S., 752
 Rothschild, P. de, 59
 Rousseau, E., 104, 370, 434, 456, 555, 804
 Rousseau, E. F., 727
 Routh, I. B., 832
 Roux, E., 692
 Rowe, R. D., 422
 Rowell, S. W., 405
 Rowinski, P., 746, 754
 Rowland, H. A., 4
 Rowley, C. D., 256, 832, 840
 Roxburgh, L., 332
 Roy, N. C., 485
 Roy, N. K., 449, 481
 Roy, S., 390
 Roy, S. C., 210
 Royds, T., 40
 Ruark, A. E., 228
 Ruben, S., 139
 Rubens, H., 6
 Rubenstein, B. B., 268
 Rubino, P., 822
 Rudberg, E. G., 451
 Ruddy, M., 708
 Ruderman, A., 620
 Rudolph, L., 853
 Rudy, H., 851, 852
 Rücker, C., 485, 491
 Rudy, R., 82, 236
 Ruehle, A. E., 64, 851
 Ruhmekorb, F., 851
 Ruess, H., 682
 Ruttenuaer, A., 142, 168, 175
 Ruggli, P., 471
 Ruhemann, M., 294
 Ruinskaya, E. S., 253
 Rump, W., 342, 355
 Rundle, G. W., 577
 Runge, C., 293
 Runkel, K., 530
 Runtzo, P. M., 408
 Rupe, H., 476
 Rupe, I. W., 786, 853
 Rupert, F. F., 644
 Ruppert, W., 718
 Ruppel, E., 458, 798
 Ruschig, H., 689
 Rуска, J., 124
 Rusleitner, K., 662
 Russ, S., 693, 694, 697, 706
 Russanow, A., 64
 Russell, A. S., 405
 Russell, E. E., 560
 Russell, E. H., 715, 772
 Russell, E. J., 286
 Russell, G. R., 783
 Russell, H. N., 24, 192
 Russell, W. C., 175, 787, 814, 838, 856
 Russell, W. K., 715, 769, 772
 Rutherford, Lord, 21
 R. U. V. Engineering Corporation, 829
 Ruzicka, L., 809
 Rabinin, G., 288
 Ryd, S., 449, 450
 Rydberg, 20, 22, 23
 Rydholm, M., 792, 822
 Ryde, J. W., 52, 74, 142
 Ryerson, L. H., 258

- Rygh, A., 849
Rygh, O., 804, 809, 812, 815, 817, 849
- S**
Sabalichschka, T., 867
Sabatelli, V., 499
Sacchi, U., 754
Sacharoff, G., 860
Sachs, D., 369
Sachs, F., 472
Sachse, H., 301, 310
Sacki, K., 860
Saha, M. N., 48, 193, 337
Saha, N. K., 396
Sahay, V., 546
Saidman, J., 733, 762, 776
St. John, C. E., 50, 192
St. Julian, R. R., 848
Saint-Maxen, A., 479
Saito, S., 608, 621
Saito, Z., 857
Sakai, S., 530
Sakuma, L., 586
Sakurai, S., 183
Saladini, G., 514
Salley, D. J., 303, 403
Salmon, W. D., 850
Salmon-Legagneur, F., 399
Salmony-Karsten, A., 169, 171, 829, 832, 840
Salo, A., 550
Salomon, H., 852
Salomon, K., 859
Salow, H., 295
Saltmarsh, M., 387
Saltmarsh, O. D., 425-427, 429-431
Salzberg, P., 592
Samant, K. M., 810, 873
Sancec, M., 435
Samokhvalova, G., 837
Sanpson, C. M., 774
Samuel, R., 240, 331, 337, 355, 395-397
Sanctis, A. G. de, 834, 841
Sandholzer, L. A., 712
Sandonnini, C., 443, 469
Sanford, H. N., 748, 825
Sannicé, C., 188
Sanyal, R. P., 869
Sanzo, L., 432, 710
Sapozhnikov, D. I., 881, 882
Sarkar, P. B., 550
Sarkaria, A. R., 350
Sasaki, N., 274, 344
Sass, R. B., 395
Sassmann, H., 447
Sato, M., 573
Sattler, L., 447, 541
Savard, J., 479, 495
Savost'yanova, M. A., 378
Sawyer, R. A., 36, 42
Sayre, J. D., 888
Scagliarini, G., 514
Scal, C., 74, 359, 394, 514
Schaarchmidt, A., 506
Schachtschabel, K., 164
Schacken, J. M. G. de, 657
Schade, H., 740
Shadow, H., 744, 745
Schaefer, K., 270
Schaefer, V. J., 265
Schaefer, W., 549
Schaffner, M., 492
Schall, C., 498
Schall, L., 741
Schamberg, I. F., 756
Schamp, H. M., 763
Schanz, F., 448, 449, 675, 762, 763, 865
Scharlau, B., 823
Scharwin, W., 633
Schaum, K., 271, 388
Schaumann, H., 336
Scheele, K. W., 6
Scheer, 827
Scheibe, G., 42, 264, 337, 338, 351, 395, 396, 401, 425, 458, 593, 594, 624
Scheiber, J., 589
Scheibler, H., 541
Scheidt, E. O., 722
Scheiferle, B., 274
Schenck, C. C., 41
Schenck, F., 813, 816, 834
Schenk, P. W., 288-290, 305, 330, 385
Schering-Kahlbaum A.-G., 77, 431, 689
Scherz, F., 871
Scheunert, A., 790
Scheurer, A., 614, 638
Schieblich, M., 790, 792, 838
Schifflett, C. H., 414, 415
Schimkus, B., 804
Schindler, A., 840
Schipp, L. T., 401
Schippers, J. C., 819
Schirmer, H., 584
Schischlaiewa, S., 776
Schlägel, H., 359
Schlaer, S., 859
Schlager, M., 388
Schlayer, C., 710
Schlechter, E., 738
Schleede, A., 366, 384
Schleip, W., 718
Schlemmer, F., 562
Schlenk, F., 687
Schlenk, W., 626
Schlessinger, L., 398
Schlessinger, M., 271
Schlitter, E., 852
Jos. Schlitz Beverage Co., 722
Schlivitch, S., 503
Schlotthauer, C. P., 861
Schlubach, H., 432
Schlutz, F. W., 792, 794, 801, 830
Schmallfuss, H., 553, 559, 740
Schmick, H., 49
Schmid, H., 248
Schmid, R., 308
Schmidlerer, L., 476
Schmidlin, J., 626
Schmidt, G., 271, 882
Schmidt, H., 447
Schmidt, H. J., 541
Schmidt, H. O., 826
Schmidt, J., 624, 689
Schmidt, K., 174
Schmidt, M., 856
Schmidt, M. E. A., 657
Schmidt, M. P., 648
Schmidt, O., 809
Schmidt, R., 378, 454, 455
Schmidt, R. W., 48
Schmidt, W., 92
Schmidt-Nielsen, S., 684
Schmidy, A., 124
Schmitt, P., 396
Schmitz and Co., 547
Schmitzler, E., 532
Schmorl, G., 778
Schmutz, F. C., 175, 556, 578, 580
Schmutz, R., 346, 539
Schneegg, H., 720
Schneider, E., 263
Schneider, E. G., 7
Schneider, H., 183, 246, 726, 828
Schneider, M., 361, 826
Schneidewind, A., 744
Schneider, A., 480
Schoder, F., 867
Schömmmer, F., 365, 384
Schoeld, F. A., 341
Schön, M., 83, 592
Schoen, M. J., 575
Schönbein, C., 292
Schönberg, A., 464, 505, 509, 510
Schoenholz, L., 820
Schönenleber, F. C., 846
Schönrock, O., 68
Schöpp, K., 849, 852
Schotzow, R. E., 652
Schoffstall, C. W., 188
Schofield, H., 569
Schofield, R. K., 228
Scholefield, F., 616
Scholl, H., 377, 828
Scholl, R., 507, 518, 522
Scholtz, F., 483
Schoorl, N., 396
Schoppee, C. W., 493
Schopper, T., 609
Schorigin, P., 469
Schormüller, J., 445
Schott and Co., 168
Schottky, W., 84, 93
Schou, S. A., 416, 419, 431, 432, 525, 651
Schour, J., 824
Schpolaki, E., 335
Schrader, F., 376
Schreiber, E., 821
Schroeder, H., 658
Schrödinger, E., 10, 26, 226
Schroeter, G., 432, 511
Schroeter, M. P., 888
Schroter, W., 624
Schuberth, K., 690
Schübel, K., 837
Schüler, H., 26, 151, 163
Schütze, H., 410
Schuknecht, W., 792
Schuler, R., 847
Schulman, J. H., 265
Schultz, C. T., 281
Schultz, F., 851
Schultz, G., 471, 472
Schultz, O., 840, 841
Schultze, G., 589
Schultze, G. R., 312, 536
Schultzer, P., 783, 784
Schulz, H., 587, 590
Schulz, M., 579
Schulz, P., 94
Schulze, B., 26
Schulze, F., 386
Schulze, G., 612
Schulze, W. A., 656
Schulzer, P., 779
Schumacher, H. J., 296-298, 306, 307, 310-314, 316, 346, 349, 394, 395, 401, 407, 510, 526, 532, 533, 535-538
Schumacher, L., 685
Schumann, V., 7, 293
Schumm, O., 624
Schupp, E., 635
Schuster, A., 40
Schwab, G. M., 532
Schwarschild, K., 220
Schwarz, F. K. T., 860
Schwarz, H., 743
Schwarz, M., 404
Schwarz, R., 332, 333, 363, 368, 376
Schwarzenbach, G., 849
Schweckendiek, C., 479
Schweinitz, H. D. von, 357
Schweitzer, E., 42, 662
Schweitzer, H., 284
Schwenk, E., 431, 514
Schwerin, K., 674, 675
Schwob, M., 450
Scimone, V., 758
Scott, G. H., 822
Scott, H. T., 836

- Scott, J. R., 608
 Scott, K. G., 865
 Scott, W. D., 474
 Sears, H. J., 727
 Sears, W., 131
 Seberger, M. V., 818
 Secarcanu, S., 475
 Secchi, C., 733
 Seceroy, S., 744
 Seed, L., 823
 Seel, H., 766
 Seel, P. C., 591
 Seeliger, R., 48, 49, 82, 83
 Seeling, K., 838
 Seibert, F. B., 690
 Seide, J., 718
 Seide, O., 503
 Seitz, E. O., 857
 Seitz, F., 265, 375, 385
 Selden Co., 481, 545
 Seldeslacht, A., 757
 Seligsohn, F., 685
 Sellards, S. W., 862
 Semashko, V., 837
 Semb, J., 617
 Semenov, N., 214, 303, 340
 Semmens, E. S., 267, 268, 882
 Semp, H., 522
 Sen, H. K., 682, 684
 Sendlinger Optischer Glaswerke, 167, 171
 Senfitehen, H., 231, 257, 302
 Senftner, G., 660
 Sen-Gupta, D. N., 550
 Sen-Gupta, P. K., 324, 395
 Sen-Gupta, S. B., 624, 625
 Serfass, E. J., 651
 Servigne, M., 142, 152
 Seshacharyulu, E. V., 350
 Seshadri, T. R., 488, 503
 Setz, P., 808
 Seuss, A., 552
 Sexton, W. A., 804
 Seybold, A., 870, 888
 Seyderhelm, R., 748
 Seyewetz, A., 365, 495, 499, 633
 Seymour, M. W., 485
 Shanassy, H., 869
 Shapiro, C. V., 164, 466
 Shaposhnikoff, A., 31, 82
 Sharf-ud-Din, 396
 Sharma, B. S., 358
 Sharma, R. S., 304, 339
 Sharp, D. G., 695
 Sharp, J. F., 328, 329
 Sharp, P. F., 848
 Sharp, W. E., 531
 Sharpless, G. R., 704
 Sharvin, V. V., 615
 Shattock, F., 741
 Shaver, W. W., 294
 Shaw, H. F., 789
 Shear, M. J., 785, 792, 822, 823
 Sheard, C., 167, 512, 727, 763, 766, 788, 861, 885
 Sheboldaeva, A. D., 860
 Sheets, O., 780
 Shekhter, A., 318
 Shelling, D. H., 792, 820, 824
 Shelow, E., 804
 Shelton, H., 366
 Shenstone, A. G., 24
 Shenstone, W. A., 282
 Shepard, N. A., 601, 609, 610
 Shepherd, R. S., 581
 Sheppard, S. E., 369, 376, 377, 379-382, 679
 Sheremet'ev, G., 261
 Sherrill, M. S., 295
 Sherman, A., 812
 Sherman, E., 785, 792, 793, 836
 Sherman, H. C., 780
 Sherrill, M. L., 413
 Sherts, J. H., 411
 Shibata, K., 877, 882
 Shibata, Y., 337, 479, 670
 Shidei, J., 358
 Shidei, T., 585
 Shile, V. N., 652
 Shilov, E. A., 346
 Shimada, J., 849
 Shinohara, U., 40
 Shinozaki, Y., 573
 Shin-Piaw, C., 297
 Shipley, P. G., 779
 Shirley, H. L., 888
 Shishacow, W., 209
 Shishlovskii, A. A., 504
 Schlaer, S., 271
 Shljivic, S., 353
 Shmidt, Y., 411
 Shneer, I. M., 591
 Shoda, M., 106
 Shohl, A. T., 785, 846
 Shoji, Y., 762
 Shomura, J., 586
 Shono, T., 584
 Shorugan, P. P., 521
 Shpolskii, E. V., 261, 444, 445
 Shrader, J. H., 835
 Shrewsbury, C. L., 855
 Shrum, G. H., 853
 Shrum, G. M., 176
 Shtern, E. A., 887
 Shugladze, A. K., 860
 Shull, C. A., 867
 Shumway, E. D., 829
 Shutt, W. J., 295, 296
 Shvartz, A. S., 341
 Sibilia, C., 711, 885
 Sibiriyakova, G. N., 411
 Sickman, D. V., 459
 Sidoli, E., 746
 Sidwell, A. E., Jr., 271, 858
 Siedentopf, K., 282
 Siegel, J., 785
 Siegler-Soru, E., 352
 Siemens, W., 66
 Siemens and Halske, A.-G., 58, 135, 150
 Siemens-Schuckert Werke, 60
 Siemens-Werke, A.-G., 366
 Sieper, G., 308
 Sieplein, O. J., 581
 Sigal, F. S., 385
 Sigr, W., 476
 Siemund, F., 424, 473
 Silber, P., 393, 449, 468, 470, 474, 476, 491, 493, 496, 511, 515, 517
 Silberman, J. T., 281
 Silherrad, O., 545
 Silberstein, L., 379
 Silica Syndicate Ltd., 151
 Silverman, A., 170
 Simard, R., 627
 Simmonds, N., 779, 780
 Simmons, N. L., 333, 354
 Simola, E. J., 613
 Simon, H. T., 46
 Simon, R., 780
 Simon, W., 485
 Simona, E. I., 816
 Simonds, E., 816
 Simonis, W., 873
 Simonnet, H., 669, 750, 790, 795, 798, 819, 823, 860
 Simons, L., 209
 Simpkins, G. W., 853
 Sinclair, R. D., 747, 786
 Singer, E., 856
 Singh, B. K., 268, 515, 516
 Singh, B. N., 874, 887
 Singleton, F., 882
 Singleton, W., 51
 Sinha, P. C., 391
 Sirch, C. W., 720
 Sirian Lamp Co., 139
 Sisley, P., 645
 Six, G., 386
 Skautzinski, B., 688
 Skau, E. L., 817
 Skaupy, F., 19
 Skaupy, L., 85
 Skunner, S., 367
 Skorko, E., 273
 Skrabal, A., 276
 Skvortzov, S. S., 874
 Slator, A., 542
 Slepian, J., 32, 48, 49, 82
 Slipher, V. M., 194
 Slout, L., 304
 Slotka, K. H., 689
 Smakula, A., 373, 380, 406, 453, 488, 490, 565, 798, 799
 Small, J., 819
 Smedley-Maclean, I., 789, 795
 Smekal, A., 374
 Smelt, J. A., 171
 Smetana, H., 860, 863
 Smiles, S., 493
 Smiley, D. E., 775
 Smith, A. E., 161, 163
 Smith, A. L., 623
 Smith, A. R., 825
 Smith, A. T., 718
 Smith, A. W., 167
 Smith, C. A., 835, 838
 Smith, D. F., 210, 527, 530, 531
 Smith, D. M., 535, 662
 Smith, F. C., 711
 Smith, F. L., 855, 873, 881
 Smith, E. M., Jr., 770
 Smith, E. W., 643
 Smith, F. C., 670
 Smith, F. C., 271
 Smith, F. D., 481
 Smith, F. F. P., 457
 Smith, F. R., 42
 Smith, H. A., 299, 300, 305, 663
 Smith, H. D., 176, 358
 Smith, H. H., 779, 788, 789, 792, 795, 847
 Smith, H. P., 543
 Smith, J. B., 814
 Smith, J. H., 777
 Smith, J. H. C., 418, 419, 854
 Smith, L. A., 690
 Smith, L. E., 588
 Smith, L. L. W., 848
 Smith, L. W., 174, 789
 Smith, M. A., 653
 Smith, M. C., 856
 Smith, N. D., 161
 Smith, W., 269
 Smith, W. C., 636, 637
 Smuts, A., 206, 299
 Smull, J. G., 554, 567, 568
 Snelling, W. O., 530
 Snitter, P., 587
 Snoke, H. R., 661
 Snow, C. P., 360, 416, 424, 808, 848, 849, 854
 Snow, O. W., 882
 Snow, R. D., 407
 Snyder, C. D., 732
 Snyder, R. M., 722
 Snyder, V. D., 155
 Soames, K. M., 780, 789
 Sobel, A. F., 805, 832
 Sobel, J., 819
 Sobue, H., 617

- Soc. anon. de Saint-Gaubain,
Chauny et Cirey, 176
- Soc. anon. les usines Rémy, 829
- Soc. anon. pour les Applications
des Gaz Rares établissements
Claude-Paz et Silva, 36, 142
- Soc. d'Exploitation des Procédés
d'Impression Sardou, 599
- Soc. des usines chimiques Rhône-
Poulenc, 562, 592, 833
- Soc. Le Serment, 721
- Soc. pour l'ind. chim. Bâle, 62
- Söderbäck, E., 457
- Söderman, M., 381
- Söhngen, N. L., 710
- Söll, J., 530
- Soer, J., 846
- Soeur, J., 822
- Sohoni, N. V., 361
- Solechnik, N. Y., 562
- Sollazzo, G., 469, 471
- Solmssen, U., 854
- Solodovnik, 657
- Solomon, A. K., 466
- Solomon, S., 873
- Soltan, A., 68
- Solvay Process Co., 545
- Somerville, P. G., 656
- Sommer, H., 562, 613, 614, 623,
645
- Sommer, J. J., 46
- Sommerfeld, A., 23, 228
- Sommermeier, K., 238
- Sonkins, S., 72
- Sonne, C., 717, 734, 744, 750,
779, 782, 783
- Soos, M., 759
- Sostmann, H., 341
- Sotto, G. E. de, 357
- Souder, W. H., 107
- Souty, P., 435
- Sovalova, A., 582
- Spanner, H. J., 131, 133, 149
- Sparre, F., 530
- Speakman, J. P., 623
- Spealman, C. R., 629, 760, 862,
864, 865
- Speas, E. B., 388
- Speas, W., 624
- Speer, J. H., 805, 822
- Spence, C., 773
- Spence, D., 596
- Spence, J. C., 820
- Spence, K. C., 800
- Spence, R., 397, 427
- Spence, D. A., 647
- Spencer, L., 347
- Sperti, G., 147, 183, 246, 708,
726, 828
- Spickard, V. W., 838
- Spiegel-Adolf, M., 669, 674, 675,
677, 690, 733, 739
- Spies, T. D., 823
- Spitschka, W., 648
- Spiller, J., 601
- Spindler, H., 72
- Spinka, J., 854
- Spinks, J. W. T., 297, 298, 307,
348
- Spitta, T., 308
- Spöhr, H. A., 866, 869, 871, 874
- Spohn, H., 877
- Spolverini, L. M., 722
- Sponer, H., 228, 235-237, 242,
244, 273, 275, 282, 293, 317,
325, 330, 331, 372
- Spong, A. H., 355
- Spooner, L. W., 190
- Spranger, 821
- Sprenger, G., 296
- Spring, F. S., 805, 809, 810, 853
- Springer, J. F., 720
- Spychalski, R., 388
- Squire, G. V. V., 287, 288
- Squires, B. T., 860
- Srinivasan, M. K., 550
- Staats, E. M., 182
- Stacey, R. S., 819
- Stafford, G., 165
- Stähler, F., 674
- Stair, R., 99, 109, 147, 165, 166,
174, 175, 188, 195, 738
- Stamberger, P., 558
- Stambovsky, L., 743
- Stamm, A. J., 617
- Stammers, A. D., 103
- Stammreich, H., 78, 149, 366
- Stamsö, K. K., 828
- Stancati, A., 754
- Stanco, Inc., 562
- Standard Brands, 563, 833
- Standen, G. W., 64, 574
- Stănescu, P. P., 874
- Stange, O., 816
- Stanley, W. M., 712
- Stanfield, R., 413, 656
- Stark, J., 31, 81, 82, 147, 207,
214
- Starkie, D., 167, 169, 173
- Stasiw, O., 374
- Stateler, E. S., 720
- Staud, A. H., 64
- Stand, C. J., 591, 592
- Stauder, H., 593
- Staudinger, H., 429, 602, 603
- Staufel, J. F., 876
- Stencio, F. W. R., 127, 394
- Steudman, F., 509
- Stearns, G., 819
- Steck, I. E., 785, 822
- Stedman, H. L., 675
- Steel, C., 431, 478
- Steel, G. E., 805
- Steel, J. K., 493, 503
- Steele, C. C., 871
- Steele, G. J., 42
- Steenbeck, M., 52
- Steenbock, H., 780, 784, 785, 788-
791, 793, 801, 802, 805, 813-815,
822, 824, 827, 829-831, 836, 837,
839, 840, 846, 853, 855
- Stefan, 15-17
- Steiger, R. E., 502, 674
- Steigerwald, C., 259
- Steigmann, A., 260, 629, 632, 804
- Stein, C. P., 275
- Stein, G., 805
- Stein, H. B., 781
- Stein, J. G., 660
- Stein, N. O., 298, 307, 329, 330
- Steinbach, M. M., 773, 824
- Steinberg, A., 657
- Steinberger, F. K., 343, 483
- Steiner, A. B., 393
- Steiner, P. E., 748
- Steiner, W., 156-158, 230, 272,
279, 282, 295, 380
- Steinmetz, C. P., 46
- Stenger, E., 97, 182
- Stenström, M., 479
- Stenstrom, W., 803
- Stephen, D., 397
- Stephen, W. E., 869
- Stephens, F. I., 890
- Stephens, H., 775
- Stephens, H. C., 829
- Stephens, H. L., 883
- Stephenson, A., 464
- Sterges, A. J., 350
- Stern, A., 377
- Stern, B. E., 855
- Stern, E., 597
- Stern, H. J., 882
- Stern, K. G., 685, 851, 859
- Stern, O., 214, 272, 287
- Sterzel, S. E., 358
- Stevens, D. S., 160
- Stevens, F. A., 727
- Stevens, N. M., 718
- Stevenson, M. M., 819
- Stewart, J. Q., 2
- Stewart, K., 333
- Stewart, T. D., 529, 534, 535
- Stewart, W. D., 889
- Stieger, G., 306, 310, 312, 536
- Stiehl, K., 522
- Stiemens, H., 754
- Stiles, W., 866, 874
- Stull, E. U., 822
- Stimson, F. J., 42
- Stiven, D., 753
- Stix, E., 518, 522
- Stobbe, H., 343, 385, 396, 410,
478, 483-485, 488, 489-491, 493,
517
- Stock, A., 62, 124, 359
- Stock, L. W., 379
- Stockbarger, D. C., 34, 97, 111,
174, 176, 177, 789
- Stöckelbach, F. E., 183, 743
- Stockhausen, K., 762
- Stockmann, H., 413
- Stoeckly, J. J., 650
- Stoermer, R., 413, 438, 447, 448,
452, 455, 456, 480-483, 488,
882
- Stokes, G., 6, 207
- Stokes, J., Jr., 836, 842
- Stoklasa, J., 715, 868, 888
- Stoll, A., 867, 871, 876, 878
- Stoll, B., 101
- Stoll, W., 810
- Stolt, H., 48
- Stone, F. M., 670
- Stone, J. F. S., 547, 883
- Stora, C., 269
- Storch, H. H., 318
- Storey, H. H., 860
- Strachan, E. K., 153
- Strachow, N. van, 344
- Strain, D. E., 584
- Strain, H. H., 888
- Strangeways, T. S. P., 708
- Strating, J., 413
- Straus, F., 478
- Strayer, J. W., 818, 823
- Stiehl, A., 516
- Streck, E., 385
- Streeter, L. R., 890
- Streptov, N. P., 494
- Strickland, R. F., 143
- Strieter, O. G., 661
- Stringham, O. L., 841
- Strömberg, R., 376
- Strong, J., 96
- Strott, A., 888
- Struck, H. C., 742, 785, 819, 824
- Struck, H. D., 822
- Strukov, I., 497, 550
- Stuart, H. A., 257
- Stuart, P. A., 809
- Stuckardt, K., 182, 272, 274, 275
- Studienges., für Wirtschaft und
Industrie, 139
- Studnitz, G. von, 857
- Stueckelberg, E. C. G., 163, 293
- Stucklen, H., 155, 394
- Stuff, F., 45
- Stuhlman, O., Jr., 36
- Sturrock, W., 144, 147
- Stutz, G. F. A., 556, 568-571,
583, 585, 587
- Stutzke, S., 858

- Style, D. W. G., 190, 248, 250, 252, 282, 304, 399
 Subramonium, B. R., 546
 Sucharavskii, M., 472
 Suciu, M., 626
 Suckfüll, E., 805
 Sudborough, J. J., 467
 Süllmann, H., 852
 Sús, O., 872
 Sugie, J., 179
 Sugie, S., 168
 Sugihara, N., 742
 Suguiera, J., 236
 Sugura, Y., 50, 149, 163
 Suhrmann, R., 131
 Suida, H., 467, 468, 473, 481, 515
 Suirkin, Y., 254
 Sullivan, W. N., 659
 Sumi, M., 803, 807
 Summerfeldt, C., 824
 Sunder, C., 574
 Sundhoff, D., 314, 533
 Sung, T.-T., 682
 Sunzeri, G., 865
 Super, L. P., 706
 Supniewski, J. V., 860
 Supplee, G. C., 813, 814, 839, 841-844, 846, 848, 852
 Surányi, G., 709, 750
 Sure, B., 851
 Surie, E., 795
 Suryanarayana, K., 343, 348
 Sushkevitch, T., 309
 Sutherland, E. C., 723
 Suzuki, K., 759
 Suzuki, M., 505
 Suzuki, S., 172
 Suzuki, T., 183, 857
 Svedberg, T., 64, 181, 379, 386, 670
 Sventitskii, N. S., 50
 Sveshnikov, B. Y., 262, 335
 Sveshnikova, N. P., 837
 Sviridova, T. A., 706
 Swann, G., 810
 Swann, W. F. G., 713
 Sward, G. G., 580, 581
 Swartz, O., 710
 Swenson, T., 545
 Swingle, W. W., 755
 Swings, P., 168
 Sykes, J. F., 822
 Sylvania Corporation, 561, 562
 Sylvester, N. D., 559, 560, 831
 Szakáll, A., 746
 Szalay, S., 434, 435
 Szarvasy, E., 530
 Szegő, L., 624
 Szendrő, P., 673, 678
 Szigetti, B., 271
 Szillard, A., 624
 Szillard, 97
 Szörenyi, E., 863
 Szörenyi, E. T., 860
 Szulc, N., 57
 Szűts, A., 860

T
 Tabern, D. L., 832
 Taboury, M.-F., 391
 Täufel, K., 432, 553
 Tafel, J., 703
 Taher, N. A., 428
 Takagi, T., 188
 Takahashi, T., 111
 Takahashi, Y., 163
 Takamiya, E., 804
 Takata, R., 790
 Takayama, T., 683
 Takebe, T., 106
 Takei, M., 619
 Taketomi, N., 434
 Talen, H. W., 603
 Talmud, D. L., 334, 465
 Tamiya, H., 630
 Tampier, L., 423
 Tamura, A., 756
 Tamura, M., 289
 Tanaka, K., 630
 Tanaka, T., 156
 Tanaka, Y., 608
 Tănăsescu, E., 478
 Tănăsescu, H., 472
 Tănăsescu, I., 472, 475, 478, 482, 490, 516, 626
 Tanberg, R., 48, 49, 119
 Tandon, S. P., 350
 Tang, P. S., 717
 Tang, T.-H., 682
 Tangl, H., 750
 Tanino, F., 756
 Tanner, F. W., 710
 Tanner, R. R., 648
 Tannigen, F. C., 621
 Tanret, G., 795, 823, 832, 434, 436
 Tappan, C., 60
 Tappeiner, H. v., 344, 860
 Tartakowsky, P., 375
 Tasaki, T., 476, 487
 Tataranu, F., 757
 Tataranu, I., 747
 Tatnall, R., 49
 Tatum, W. W., 550
 Taub, A., 657
 Taube, H., 348
 Tauss, J., 655
 Tautini, E., 742
 Taverne, N., 573
 Tawde, N. R., 364
 Taylor, A., 60
 Taylor, A. H., 147, 179, 181, 642, 738
 Taylor, A. M., 383
 Taylor, A. W. C., 272, 275
 Taylor, B. S., 610
 Taylor, E. M., 165
 Taylor, H. A., 459, 460, 504
 Taylor, H. S., 86, 125, 150, 156, 212, 257-259, 284, 301, 303, 310, 313, 317, 319-323, 340, 394, 397, 403, 406-408, 410, 414, 415, 422, 427, 439, 458, 464, 488, 683
 Taylor, J. S., 51, 97
 Taylor, M. W., 814, 856
 Taylor, N. B., 818, 822
 Taylor, W., 182, 246
 Taylor, W. C., 166
 Tchakhotine, S., 704, 717
 Teagarden, E. J., Jr., 523, 865
 Tear, J. D., 6
 Tedde, K., 363, 368
 Teele, R. P., 193
 Teft, R., 391
 Teichler, G., 674
 Teichmann, C. F., 531
 Teindl-Czech, L., 709
 Teller, E., 236, 240, 244, 330, 331, 375
 Templin, V. M., 822, 824
 Tenchio, F., 740
 Tennant, R., 681
 Teplov, I., 750, 865
 Terata, B., 689
 Terenin, A., 190, 231, 238, 240, 241, 263, 345, 402, 438, 439, 464
 Tern, R., 554
 Terrien, J., 382
 Terroine, E. F., 681
 Testi, G., 620
 Tetzner, E., 756
 Teves, M. P., 241
 Thacker, E. A., 826
 Thalman, R. R., 786
 Thatcher, L., 822
 Thayer, R. N., 142
 Thayer, S. A., 856
 Thee, W. C., 663
 Theiler, A., 783
 Theiss, E. R., 651
 Theobald, Mille., 781
 Theorell, H., 670, 688, 853, 857
 Thermal Syndicate, 147, 151
 Thibaut, J., 8
 Thiele, H., 299, 308, 333, 693, 698
 Thiele, W., 810
 Thiessen, P. A., 389
 Thoenes, F., 822
 Thomas, A., 109
 Thomas, B. H., 813, 822, 830, 835, 837-839
 Thomas, J., 687
 Thomas, F. H., 77
 Thompson, A., 76
 Thompson, E. G., 618
 Thompson, H. E., 804
 Thompson, H. W., 333, 334, 423, 425, 426, 460, 461, 464, 854
 Thompson, L., 727
 Thompson, W. P., 77
 Thompson, W. R., 681, 683, 765
 Thomson, D. L., 819
 Thomson, E., 151
 Thomson, G. P., 11
 Thomson, J., 32
 Thomson, J. C., 564
 Thomson, J., 269, 287
 Thomson, R. F., 550
 Thomson Research Laboratory, 151
 Thon, N., 281, 287
 Thoracius, R., 8
 Thornton, W. N., 95
 Thorpe, J. F., 541
 Thourret, W., 94
 Thovet, J., 381
 Thovet, J. F., 381
 Thunberg, T., 877
 Tian, A., 73, 206, 299, 339
 Tichalskaya, V. V., 849
 Tiede, E., 366, 793
 Tiedemann, W., 546
 Tietze, E. L., 422, 423
 Tietze, E., 183
 Tietze, W., 109
 Tiggelen, A. van, 320
 Tüllisch, H. C. E., 827
 Tingey, H. C., 156, 230, 272, 275
 Tingley, S. L., 655
 Tisdall, F. F., 170, 782, 824, 830, 837
 Titeica, R., 511
 Titoff, A., 357
 Titov, A. I., 470
 Tittel, H., 209
 Tittler, R. P., 704
 Titus, H. W., 787, 814
 Titus, R. W., 787, 854
 Tival, H., 727
 Tixier, G., 798, 829, 832
 Tkachev, A. D., 560, 573
 Tobey, J. A., 835
 Tobin, E., 492
 Tobiska, J. W., 856
 Toczyski, T., 754
 Todd, C., 860
 Todd, T. W., 818
 Töpelmann, H., 792
 Toepfer, K., 410
 Török, L., 741
 Tognoni, C. A., 587
 Togo, S., 94
 Tokumitsu, Y., 749
 Toldte, W., 580, 581

- Tollman, J. P., 51
 Tolloczko, S., 393, 394, 526
 Tolman, R. C., 209, 210, 247, 249, 250
 Tompkins, H. K., 530
 Tompkins, R. G., 722
 Toni, G. de, 732, 754
 Tonks, L., 81, 83, 84, 94
 Tonnet, J., 756
 Tonney, F. O., 835
 Topchiev, A. V., 470, 521
 Topley, W., 776
 Toporetz, A., 378
 Toriyama, Y., 40
 Tottingham, W. E., 883, 887, 888
 Toul, F., 415
 Townsend, R. V., 306
 Toy, F. C., 377, 379
 Toyabe, Y., 611
 Toyama, J., 686
 Toyoda, G., 749
 Tracy, G. P., 523
 Trajtenberg, S., 744
 Tramm, H., 286, 308
 Tranin, S., 722
 Transeau, E. N., 866
 Trautmann, G., 795, 796, 813
 Trautz, M., 209, 255, 274, 316, 331, 332
 Trebler, H. A., 840
 Treibs, W., 515, 516
 Trehana, F. C., 870
 Trehin, R., 343
 Trelease, S. F., 882
 Trevorrow, V. E., 824
 Trevy, P., 592
 Tricault, G., 823
 Triebold, H. O., 840
 Trifonoff, A., 288
 Trifonov, N., 444
 Trillat, J. J., 376
 Trischmann, H., 484
 Tristan, F., 178
 Trivedi, H., 275, 281
 Trivédi, R., 482
 Trivelli, A. P. II., 376, 379, 380
 Trolliet, A. L., 587
 Trotman, S. R., 188, 621
 Trotskii, V. L., 706
 Trufanov, A. V., 832
 Truffault, R., 532
 Tsai, L. S., 456
 Tschentke, H. L., 572
 Tshubarov, R., 240
 Tsirog, I., 93
 Tsi-Zé, N., 297
 Tsuchida, R., 368
 Tsuge, H., 849
 Tsukamoto, K., 338
 Tuchel, H., 346
 Tüenter, J. P. A., 346
 Türkenburg, F. R. von, 73
 Tuffail-Malkana, M., 522
 Tully, W. C., 814
 T'ung, T., 860, 865
 Tupholme, C. H. S., 624
 Turek, O., 472
 Turner, A. A., 720
 Turner, E. E., 546
 Turner, H., 609
 Turner, J. S., 644
 Turner, L. A., 24, 83, 231, 243, 257, 273, 275
 Turner, W. E. S., 167, 169, 171, 173
 Tweedy, W. R., 754
 Twyman, F., 271, 853
 Tyndall, E. P. T., 155
 Tyndall, J., 205
 Tzoni, H., 817
 Uchimura, T., 760
 Ueda, H., 671
 Uehara, K., 683
 Ugo, A., 734, 766
 Uhlenbeck, G. E., 25
 Uhlmann, E., 734, 738
 Ulbrich, W., 75
 Umesawa, H., 621
 Ungar, G., 383
 Unger, L. J., 778, 779, 783
 Unger, W., 287, 288
 Universal Oil Products Co., 652
 Unsöld, A., 94
 Untersuchungs und Forschungs-Laboratorium für Lacke und Farben, 589
 Uppal, H. L., 249, 253, 486, 540
 Uraki, J., 817
 Uraki, Z., 670
 Urbach, E., 743
 Urbach, F., 861
 Urbain, E., 74, 359, 394, 514, 539
 Urban, 42
 Urban, F., 741
 Urban, F. F., 672
 Urban, O., 883
 Urbanczyk, W., 431, 432
 Ure, W., 210
 Urev, H. C., 25, 158, 159, 210, 228, 243, 303, 307, 327, 339
 Urmston, J., 280
 Urmston, J. W., 536
 Ursprung, A., 715, 873
 Urushibara, Y., 817
 Ushakov, S. N., 591
 Usher, F. L., 868
 Utaka, S., 550
 U. V. Generator Corp., 58
 Vacek, T., 688
 Vadimov, M., 720
 Vadimov, V., 837
 Vagedes, H., 721
 Vahle, W., 101, 737-739
 Vahlquist, B., 822
 Vaidya, B. K., 188, 453, 456, 522
 Vaidya, B. M., 484, 488
 Vail, C. E., 856
 Vaillant, P., 368
 Valdigué, A., 407, 432, 525
 Valenta, E., 168
 Valentin, H., 732, 885
 Valyashko, N. A., 479
 Vanev, G. M. de, 787
 Van den Berg, L. M., 396
 Van der Hulst, 565
 Van der Linden, T., 543, 544, 547
 Van der Lingen, 44, 693, 694, 698
 Van de Walle, H., 412
 Van der Ziel, A., 447
 Van Dyk, A., 409, 410
 Van Eekelen, M., 817
 Van Houten Co., 831
 Van Itallie, P. H., 743
 Van Leersum, E. C., 831
 Van Niel, C. B., 881
 Van Recsey, E., 829
 Van Recsey, N., 81, 829
 Van Sa l, R. H., 81, 829
 Vanselow, W., 377, 382
 Van Stolk, D., 797
 Van't Hoff, 206
 Van Veen, A. G., 873
 Van Vleck, J. H., 19
 Van Voorhis, C. C., 82, 83, 293
 Van Wijk, A., 115, 799, 801, 803, 805-808, 815, 829, 833
 Van Wyk, A., 171
 Van Zuydewijn, E. de R., 413
 Varadanam, C. I., 259
 Varahalu, K., 268, 367
 Varahalu, T., 367
 Varela Fuentes, B., 822
 Varetton, E., 869
 Vargin, V. V., 171
 Vailey, W. M., 179
 Varma, P. S., 546, 550
 Varshaver, G. S., 747
 Vartanyan, A. T., 259
 Vasarhelyi, J., 744
 Vashist, S. D., 617
 Vasilief Sinzova, A., 369
 Vassy, E., 152, 193, 297
 Vatter, H., 83, 93
 Vaughan, W. E., 295
 Vacchiotti, L., 468, 470, 496
 Vedder, A., 756
 Vellinger, E., 651, 654
 Velluz, L., 508, 511
 Velluz, Mme., 508
 Venar, Y., 818
 Vendor, A., 638
 Venkataramaiah, Y., 284
 Verda, D. J., 689
 Verdollin, J., 689
 Vereinigte Chemische Fabriken Kreidl Heller & Co., 508
 Verhoeff, F. H., 763
 Vermes, M., 709, 750
 Vermeulen, D., 48, 52, 877
 Vernon, A. A., 410, 488
 Veronita, M., 708
 Verreries de Goetzenbruck, 167
 Veselkin, N. V., 849
 Vesper, H. G., 532
 Viale, G., 260, 733, 849
 Vickery, H. B., 884
 Victor, E., 346
 Vieweg, A., 42
 Vignard, 784
 Vignon, L., 613
 Viktorin, O., 479
 Vila, A., 580
 Vilenkin, M., 832
 Villard, 7
 Villard, P., 209
 Villars, D. S., 182, 190, 224, 228, 352-354, 456
 Villemaine, F., 370
 Vincent, J. H., 120
 Vines, H., 755
 Virasoro, E., 684
 Virden, C. J., 484
 Virtanen, A. I., 849
 Visser, G. H., 236, 238, 476
 Vita, N., 254, 255, 344, 441, 443, 485
 Vitalite Co., 173
 Viterbe, E., 364
 Vitoria, A. P., 431
 Viñes, F., 441, 651, 670, 734, 764, 766
 Vodar, B., 349
 Voegel, W., 96
 Voelker, 151
 Voet, J., 712
 Vogel, 381
 Vogel, H., 435
 Vogele, A. C., 888
 Vogelei, L., 722
 Vogels, H., 264, 352
 Vogler, H., 376
 Vogt, K., 273
 Voigt, J., 387
 Vöitz, W., 836
 Volbert, F., 271, 351, 495, 564, 565
 Volker, H., 744, 745
 Volklinger, H., 94, 412, 670
 Vollgraff, J. A., 473, 513, 514

- Vollmann, H., 586
 Vollmer, H., 783
 Volman, D., 420
 Volmar, 246, 402, 441, 448, 450, 454, 538
 Volmer, M., 58, 60, 209, 214, 272, 287, 376, 505
 Völitz, W., 790
 Volz, K., 643
 Vore, H. B. de, 592
 Vorländer, D., 193, 485, 492, 869
 Vorozhtzov, N. N., 501
 Vorster, D., 860
 Voss, A., 411
 Voznava, A., 837
 Vranek, J., 368
 Vries, H. de, 361

Wachholtz, F., 454, 455
 Wackerlin, E., 443
 Waddell, J., 814, 834, 838
 Wadhera, M. L., 434
 Wadsworth, A., 690
 Waale, A. de, 456, 589
 Waentig, P., 613
 Wagner, C., 207, 297, 306, 311, 313
 Wagner, H., 577, 582-584
 Wagner-Jauregg, T., 314, 851
 Waguet, P., 111
 Wahl, A., 617, 638
 Wahl, H., 381
 Wahlberg, H. E., 618
 Wait, R., 817
 Wakeham, C., 523
 Wakeman, A. J., 884
 Wakkie, J. G., 871
 Waksman, S. A., 351
 Wald, G., 857-859
 Waldbauer, L., 216
 Waldie, A. T., 317
 Walker, O. J., 360, 431, 440
 Walker, P. H., 579, 581
 Walker, R. D., 381
 Walker, T. T., 823
 Walkoff, E., 820
 Wall, F. J., 556
 Wallace, J., 306, 307
 Wallach, O., 473
 Waller, M. D., 734, 741
 Wallis, G., 835
 Wallraff, A., 32
 Walls, H. J., 182
 Walsh, J. F., 173
 Walter, C., 555
 Walter, E., 467, 796, 797
 Walter, H., 558
 Walther, P., 580, 605
 Walters, E., 254, 446
 Walters, F. M., Jr., 50
 Walther, H., 662
 Walther, R. v., 493
 Walther, T., 387
 Waltner, K., 791
 Walton, J. H., 365
 Wansbrough-Jones, O. H., 356, 437, 438
 Waran, H. P., 77
 Warburg, E., 43, 44, 210-212, 214, 215, 246, 272-275, 288, 292, 294, 297, 318, 321, 342, 352, 353, 355, 453
 Warburg, O., 333, 687, 688, 732, 853, 874-876, 879
 Ward, H. K., 750
 Ward, H. M., 692
 Warde, F. M., 165
 Wardle, G. C., 636
 Warga, M. E., 98, 99, 201
 Warkany, J., 818
 Warning, E., 310, 313
 Warmoltz, N., 131
 Warmuth, K., 52
 Warren, D., 273
 Wartenberg, H. v., 249, 349
 Warweg, E., 819
 Washburn, M., 209
 Washburn, R. G., 841
 Washburne, R. N., 210
 Wasicky, R., 556
 Wassermann, A., 453
 Wassiljewa, A., 281, 387
 Wassink, E. C., 877, 881
 Wasteneys, H., 680, 683, 684
 Wastl, H., 760
 Watanabe, A., 260, 882
 Watenpugh, J. T., 818
 Waterman, H. I., 411
 Watkins, J. S., 289
 Watson, H. E., 367, 467, 468, 474, 522
 Watson, H. L., 151, 818
 Watson, M. B., 848
 Watson, W. H., 161
 Watson, W. W., 273, 330
 Watta, H. G., 417, 418, 426, 474
 Watters, B. D., 116
 Watteville, C. de, 35
 Wawilow, S. J., 262
 Way, 66
 Wearham, J., 847
 Welch, C. N., 421
 Webb, D. A., 64
 Webb, J. H., 271, 374, 376, 377, 381
 Webb, W. W., 347, 442
 Weber, A. E., 507
 Weber, K., 263, 351, 445, 522, 631, 871
 Weber, P., 526
 Webster, A., 102
 Webster, H. G., 334
 Webster, S. B., 135
 Webster, T. A., 695, 788, 792, 794, 798, 800, 801, 803-806, 821, 822, 853, 867-869, 882
 Weckel, K. G., 829, 835, 840, 841, 845
 Weedon, H. W., 555
 Wegmann, E., 331
 Weger, M., 517
 Wegmann, T., 679
 Wegscheider, R., 251, 475
 Wehnelt, A., 131, 133
 Weichmann, H. K., 183
 Weickart, F., 646
 Weidenbaum, B., 529, 534
 Weidert, F., 168, 178
 Weidlich, G., 807, 821, 832
 Weigel, O., 359
 Weigert, F., 69-71, 216, 266, 282, 284, 286, 297, 314, 341, 379, 383, 474, 475, 504, 505, 523, 524, 857, 877
 Weightman, H. E., 607
 Weingeroff, M. A., 156
 Weinhouse, S., 817
 Weinstein, I., 700, 701, 716
 Weinstock, M., 773, 779-781, 785, 788, 789, 791-794, 803, 836
 Weisbecker, H., 860
 Weisberg, S. M., 852
 Weiser, H. B., 385
 Weiss, H., 368
 Weiss, J., 261, 263, 264, 360, 370, 463, 630, 631, 871, 872, 881
 Weizel, W., 83, 163, 228, 833
 Weizmann, C., 403, 671, 672
 Welch, H., 690, 720, 725
 Welch, J. W., 826
 Weld, C. B., 818, 822
 Weld, H. W., 172
 Welge, H. J., 321
 Wellburn, E. R., 404
 Wellmann, M., 172, 380
 Wells, A. A., 558, 568
 Wells, D. A., 68
 Wells, M. W., 731
 Wells, W. F., 712, 731
 Wels, P., 676-678
 Welsh, J. H., 865
 Weltner, M., 670, 853
 Wendt, B., 562
 Wendt, G. von, 817
 Wendt, G. L., 284
 Wenger, W., 757
 Wenig, K., 676
 Wenner, R. R., 321, 323
 Werder, F. von, 804, 807, 808, 814, 816
 Werle, E., 691
 Werner, E. A., 358
 Werner, G., 648
 Werner, H., 553, 559
 Werner, O., 867
 Werschen-Weisserfeldser Braun-kohlen A.-G., 653
 Werthan, S., 578
 Wessely, F., 515
 West, D. L., 179
 West, E. S., 867
 West, H. D., 541
 West, H. I., 539
 West, W., 244, 260, 262, 280, 336, 397, 398
 Westbrook, A., 715, 885
 Westbrook, M. A., 715
 Westhaver, J. W., 31, 327
 Westin, G., 849
 Westinghouse Electric and Manufacturing Co., 74, 724
 Westinghouse Lamp Co., 139, 140
 Westphal, K., 804
 Westra, J. J., 689
 Weyde, E., 105, 628, 629
 Weygand, F., 852
 Weyl, T., 183
 Wheatstone, C., 66
 Whipple, D. V., 836, 842
 Whitaker, M. D., 36
 White, B. B., 585
 White, H. L., 25
 White, P. C., 545, 550
 Whitehead, H. R., 762
 Whitley, E., 881, 882
 Whitmore, W. B., 645
 Whittah, C. H., 852
 Whittaker, C. M., 624
 Whittier, C. C., 832
 Wichart, 472
 Wickman, P. A., 562
 Wickwire, G. C., 752, 763
 Wiebe, R., 217
 Wiedemer, C., 748, 774
 Wiedemann, G., 92
 Wiegand, C., 183, 743
 Wiegand, K., 137, 142, 840
 Wiegel, E., 388
 Wieland, 827
 Wieland, H., 444, 490
 Wieland, K., 330
 Wien, W., 15-17
 Wienands, A., 493
 Wiener, C., 785
 Wiener, H., 703
 Wiersma, C., 764
 Wierzuchowska, J., 670
 Wiesler, K., 425
 Wiesner, R., 698
 Wietzel, G., 439
 Wietzel, R., 439

- Wiggam, D. R., 591
Wightman, E. P., 379
Wig, E. O., 318-322, 399, 536, 537
Wijnand, P. C., 597
Wilbur, P., 497
Wilcox, D. E., 814, 838
Wild, G. L. E., 431, 440
Wild, W., 397, 427
Wilder, R. M., 788
Wilder, W., 838
Wildermann, M., 206, 311
Wilhelm, H. A., 64
Wilke, P., 643
Wilkie, J. B., 853
Wilkins, L., 784, 785
Willard, J., 535
Willemart, A., 508, 509
Willenberg, H., 35
Willi, E., 480
Williams, C. H. M., 824
Williams, D. M., 488
Williams, E. G., 344
Williams, I., 602
Williams, J. G., 615
Williams, J. J., 581
Williams, J. M., 447
Williams, R. R., 479, 480, 851
Williams, T. G., 449, 516
Williamson, R., 497
Williamson, W. O., 386
Willmott, S. G., 785, 854
Willis, H. S., 772
Wilmanns, G., 183
Wilsing, J., 152
Wilson, A. H., 372
Wilson, D. A., 104, 444
Wilson, E. D., 98, 155
Wilson, F. J., 490, 491, 493, 494
Wilson, G. H., 142
Wilson, I. H., 587
Wilson, I. D., 123
Wilson, L. T., 838
Wilson, W., 51, 377
Willstatter, R., 863, 867, 871, 875, 876, 878, 879
Wimmer, C., 556
Winans, J. G., 36, 95, 163
Winchester, 194, 195
Windaus, A., 792, 795, 796, 801, 803, 810, 812, 813, 816, 821, 832, 834, 862
Winderlich, R., 124
Wingchen, H., 476
Wingfoot Corporation, 612
Winkler, C. A., 427
Winn, A. G., 446
Winninghoff, W. J., 77
Winship, W. W., 151
Winter, E., 283
Winterstein, A., 854, 856
Wintersteiner, O., 851
Winther, C., 105, 107, 173, 179, 182, 210, 253, 255, 270, 305, 344, 361, 367, 370, 441, 444, 448
Winthrop Chemical Co., 659, 833, 834
Winzor, F. L., 502
Wirick, A. M., 815, 822, 831, 855
Wirth, C., 653
Wisconsin Alumni Research Foundation, 827
Wishcenus, W., 454, 493
Wiskott, A., 821, 822
Withrow, L., 663
Withrow, R., 184, 186, 726, 828
Witmer, E., 217
Witt, O. N., 626
Wittgenstein, A., 764
Wittka, F., 563
Wittstein, G., 205
Wix, A., 660
Wlodek, J., 871
Wobbe, D. E., 441
Wöber, A., 890
Wodlinger, M. H., 847
Woelffer, E. A., 838
Woerner, H. B., 60
Wohl, K., 879, 881
Wohl, Mlle., 495
Wohlgemuth, J., 742, 863
Wokes, F., 785, 854
Wolf, 386
Wolf, C. E. de, 885
Wolf, E., 460
Wolf, G., 626
Wolf, J., 169, 436
Wolf, K., 693, 698
Wolf, K. L., 163, 416, 425, 467
Wolf, L., 124
Wolf, M., 876
Wolffers, F., 366
Wolff, H., 176, 330, 576, 586, 587, 589
Wolff, K., 314, 532
Wollaston, W., 6
Wollmann, E., 588
Wollner, F., 171
Wollner, R., 171
Wölpert, K., 849
Wolter, E., 806
Woo, S. C., 414
Wood, A. R., 176
Wood, B. G., 514
Wood, B. J., 542
Wood, H. P., 663
Wood, J. G., 874
Wood, R. W., 7, 86, 109, 178, 190, 257, 467
Wood, W. C., 273, 336, 345
Woodhouse, J. C., 524
Woodroffe, D., 651
Woodrow, J. W., 556, 709, 853, 854
Woods, G. M., 487
Woods, H. J., 679
Woog, P., 555, 656
Wormall, A., 757, 758
Wörner, A., 830
Wotherspoon, R., 658
Wrede, B., 155
Wrede, F., 673
Wright, P., 115, 165
Wright, R., 273
Wright, S., 803
Wright, W. H., 718
Wright, W. L., 620
Wulf, 9
Wulf, O. R., 193, 294-296, 327
Wulf, T., 35
Wulff, P., 364
Wunderlich, W., 816
Wurmser, R., 213, 339, 425, 435, 874, 881, 882
Würth, K., 568, 576
Wurzinger, S., 820
Wyat, L., 825
Wyckoff, R. W. G., 705-708
Wyman, E. T., 174, 782, 789, 835, 838, 839
Wynd, F. L., 688, 710, 888, 889
Wyneken, I., 155
Wyrobek, O., 478, 479, 482
Wyszewianski, L., 617
Yajnik, N. A., 249, 253, 390, 434, 486, 540, 870
Yakota, S., 751
Yakushiji, E., 877
Yamafuji, K., 685
Yamagishi, T., 851
Yamaguchi, T., 619
Yamamoto, E., 625
Yamamoto, R., 851
Yamanaka, G., 757
Yamanaka, T., 495
Yamashiki, H., 681
Yamashita, S., 553, 625
Yamazaki, T., 607
Yampolskii, B., 179
Yanagihashi, T., 584
Yankin, G. M., 31
Yao, Y. T., 82
Yarnold, E. T., 404
Yeremenkow, N. P., 794
Yoda, G., 506
Yoder, L., 794, 804, 813
Yokayama, K., 790
Yoshine, S., 745
Yoshitomi, M., 818
Young, C. H., 189
Young, F. E., 855
Young, F. G., 809
Young, K. W., 250, 443, 446
Young, T., 3, 4, 6
Yovanovitch, A., 745
Zadov, V. D., 390
Zaeppfel, H., 748
Zagulin, A. V., 291
Zahn, R., 648
Zahour, R. L., 179
Zaidan-Hojin Aoyagi Kenkyisho, 143
Zaidan-Hojin Rikagaku Kenkyujo, 183
Zakowski, J., 388
Zamfirescu, G., 460
Zanetti, G., 468, 470, 496
Zavadovskii, M., 837
Zchodro, N., 632
Zdobnicki, W., 868
Zé, N. T., 156, 157, 163
Zecher, G., 139, 829, 832
Zehender, F., 852
Zeidler, G., 580, 587, 589
Zeile, K., 685
Zeise, H., 217
Zeiss, C., Co., 167
Zeiss, Ikon A.-G., 60
Zel'dovich, P. Y., 588
Zeller, H., 709
Zemansky, M. W., 92, 257
Zenghalis, C. D., 308
Zernik, F., 183
Zevland, J., 823
Zeyneck, R., 751
Zhalkovskii, B. G., 267
Zhukov, I., 411
Zhukova, A., 582
Zia, S. H., 860, 865
Ziegler, M. R., 792, 794, 830
Ziegler, W., 171, 172
Ziegler, Z., 865
Ziegler-Wellmann, M., 759
Ziersch, G., 626
Zifter, F., 530
Zikes, H., 865
Zilg, W., 444
Zilva, S. S., 848, 854
Zimmer, K. G., 475
Zimmerli, A., 173
Zimmerman, A., 471
Zimmermann, W., 105, 628, 629, 833
Zinov'ev, A. A., 559
Zmlt, E., 366, 624
Ziskin, M., 309

- | | | |
|------------------------|--------------------------------|-----------------------|
| Zlatarov, A., 554 | Zschacke, F. H., 671 | Zuckerstein, E., 755 |
| Zmanovskaya, L. I., 31 | Zscheile, F. P., Jr., 271, 870 | Zueva, R. V., 588 |
| Zocher, H., 266, 383 | Zschimmer, E., 168 | Zuithoff, A. J., 413 |
| Zolcin-ki, J., 350 | Zschoch, F., 483, 517 | Zurukzogl'u, S., 792 |
| Zondek, B., 689 | Zuber, K., 227 | Zussman, H., 858 |
| Zouckermann, R., 37 | Zucker, T. F., 816, 824, 838 | Zwaardemaker, H., 513 |

Subject Index

Abscesses, 825

Absorption bands, and optical rotation, 266
 coefficient, 207, 271
 curve, 271
 of light, and dissociation, 227
 of light by gases, 179, 285
 of light, effects due to various wave-lengths, 208
 of light, laws, 206
 spectra (see Spectra)

Acummine, 710

Accelerated tests (see Tests, accelerated weathering)

Accelerators, 252, 365, 648
 for rubber, 596, 598-601, 605, 610

Acceptors, 211, 863, 864, 871, 872
 in dye bleaching, 263, 264

Acenaphthene, 511

Acenaphthenequinone, 603

Acetal, 416, 709

Acetaldehyde, 452, 481, 595, 868
 absorption spectrum, 416, 418-420
 fluorescence, 419
 formation, 396, 397, 402, 422, 429, 431, 448, 449, 672, 676
 photoreactions, 417-423, 425

Acetaldehyde, dimethyl, 421

hexahydrophenyl, 424, 473

phenyl, 424, 473

trimethyl, 421

Acetaldol, 425

Acetamide, 340, 438, 647

Acetanilide, 340, 438, 495, 657

Acetates, 377, 536, 681

Acetic acid, 184, 340, 418, 617

absorption spectrum, 565

chlorination, 540

formation, 404, 422, 425, 428, 431, 441, 447, 449, 451, 514, 515
 photoreactions, 437, 438

Acetic acid, bromo, 451

chloro, 249, 451, 452, 540, 594

phenyl, 478

Acetic anhydride, 473, 540

Acetoacetic acid, 362

Acetoin, 421, 451

Acetol, 173, 518

Acetone, 340, 357, 362, 421, 433, 510, 514, 562

absorption spectrum, 425-428

and ethylene polymerization, 408

and lens proteins, 763

dicarboxylic acid, 362

dihydroxy, 339, 404, 428, 432

dissociation, 244

formation, 396, 402, 404, 429, 431, 450

in detection of pyridine, 521

methylene blue reaction, 102, 103, 105

nitrosoisopropyl, 461

oxidation, 425

photolysis, 397, 420, 425-428

reaction with butanol, 403

reaction with terpene alcohols, 514

sensitizer of ether photolysis, 405

Acetonuria, 752

Acetophenone, 340, 344, 430, 477

anisal, 478

amino, 498

benzaldehyde condensation product, 490

carboxylic acid, 478

dimethylamino, 629

pinacol, 403

reaction with alcohols, 403

Acetylacetone, 431, 465

Acetylbenzoyl peroxide, 480

Acetyl bromide, 440

Acetylbiomondazole, 743

Acetylcarbazole, 743

Acetylcellulose, 173, 587, 591

Acetyl chloride, 440, 465, 534, 535, 540

Acetylchloroaminobenzene, 496, 497

Acetylcoumaric acid, 488

Acetylene, 393, 407, 415, 457, 537

absorption spectrum, 414

behavior in electrodeless discharge, 36

bromination, 537, 538

chlorination, 537

deutero, polymerization, 415

divinyl, 415

formation, 62, 399, 400, 406, 424, 514

oxidation, 414, 415

phenyl, 538

polymerization, 414, 415

Acetyl halides, photolysis, 440

Acetyl peroxide, 411, 431, 440

Acetylphenyltriazine, 647

Acetyl radical, 421, 427

Acetylsalicylic acid, 436

Acetyltoluene, 547

Acheson graphite, 64

Acid anhydrides, 410, 437

chlorides, 437

dyes, fading, 635, 636, 642, 644

Acidosis, 753, 754

Acids, aliphatic, 393, 437

aromatic, 480-488, 600

fatty, 553

formation in gasolines, 653, 654

halogenated, 451, 452

in fermentation, 709

in wine, 660

organic, 437-456, 648

polymerization inhibitors, 410

Acne, 742, 769

Aconite, tincture, 658

Aconitic acid methyl esters, 456

Acraldehyde, 435

Acridine, 509, 860, 862

dyes, 640, 712

phenyl, 509

Acridone, 507

Acrolein, 423-425, 669

Acrose, 402

Acrylic acids, 454, 456, 491

ester polymers, 456, 584

Acryloid, 172

Actinometers, 96, 102-105, 202, 285, 341, 369, 400, 418, 433, 443, 452, 459, 600, 653, 656, 771

Action, 18

Activated molecules, 215, 216, 260-262

Activation energy, 207, 209, 210, 245-247, 250

chlorine-sensitized oxidation of hydrogen, 289

conversion of ergosterol into vitamin D₂, 812

deuterium-chlorine combination, 290

hydrogen-bromine combination, 276-278

hydrogen-chlorine combination, 289, 291

phosgene formation, 313

reaction of atomic chlorine and hydrogen, 283, 284

reaction of hydrogen with hydroxyl, 305

reaction of O and O₂, 300, 309

reaction of O and CO, 309

Acyloln, 451

Adaptors, for therapeutic irradiation 62, 63

Additivity, of rates of photo- and thermal reactions, 248

Adenine, 699, 701, 710, 850, 851

- Adrenaline**, 433, 688, 747, 760, 761
Adsorption, of carbon monoxide on quartz, 309
 on irradiated crystals, 259
Aerosols, 464
After-effects, photochemical, 253, 486
Afterglow, dyes, 264
Aftervulcanization, 597
Agar-agar, 585, 693-695, 697, 714, 758
Agglutinin, 757-759, 775
Agglutinogens, 758
Air, absorption of ultraviolet rays, 7, 192-202
 effect on output of mercury arc, 113, 114, 116
 formation of ozone, 292
 ionization, 269, 662
 irradiated and blood pressure, 780
 irradiated and rickets, 733
 lines, in spark discharge, 41
 mass, 192, 197, 198
 sterilization, 728-731
"Aktivin," 498
Alanine, 671, 672
Alanylglycine, 436, 671
Albumin, 390, 706
 egg, 674-679, 691, 758, 759
 serum, 674-677, 862
Alcohol, allyl, 538
 amyl, 471
 benzyl, 340
 butyl, 538
 ethyl (see Ethanol)
 isopropyl (see Isopropanol)
 octyl, 658
 propyl, 538
 tribromoethyl, 658
 trinitrobenzyl, 472
Alcoholic beverages, 207, 660
Alcohols, 369, 393, 401-405, 442, 458, 507
 as inhibitors of oxidations, 314, 350, 357, 422
 as polymerization inhibitors, 410
 bleaching of ferric chloride, 361
 bromination, 538
 conversion to sugar, 870
 formation, 432, 438, 449, 526
 from gasoline, 657
 in fermentation, 709, 710
 in mercury nitrate photolysis, 353
 oxidation, 356, 357, 404, 405, 476, 477
 poly, and lithopone blackening, 385
 reaction with benzoquinone, 480
 reaction with halo-acids, 452
 reaction with ketones, 403, 404, 517
 reaction with methylene blue, 686
 reaction with quinine, 523
Aldehyde-ammonia, 605
Aldehyde-phenol resins, 584
Aldehydes, 248, 366, 393, 407, 424, 449, 464, 546
 547, 589, 727, 728
 absorption spectra, 415-417
 and aromatic thiohydrazides, 500
 and phenanthrene quinone, 482
 aromatic, 472-476
 as polymerization inhibitors, 410
 formation, 404, 415, 448, 450, 458, 461, 468,
 517, 619, 653, 673
 from secretin, 689
 in carbohydrate photosynthesis, 867, 868, 870
 in fermentation, 709
 oxidation, 422, 423
 photoreactions, 416-425
 rancidity and, 561
 reactions with quinones, 474
 reduction to alcohols, 418
 unsaturated, 423-425
Aldol- α -naphthylamine, 603, 610
Aldoketones, 430
Aldoximes, 493, 494
"Aldur," 170, 172
Alexin, 759
Alfalfa, 790, 830, 856
Algae, 713, 714, 717, 874-876, 881-883
Alizanthrene Yellow, 616
Alizarin, 603, 632
Cyanin Green G, 622
 pigments, 590
 red lake, 643
Alkali bromides, 343
 carbonate, 172
 cations, absorption spectra, 337
 chlorides, 343
 fluorides, 238
 halide crystals, 216, 265, 372, 373
 halides, absorption spectra, 238, 239, 338, 372,
 373
 halides, dissociation, 237
 halides, photolyses, 342, 343
 hydrides, in crystals, 375
 metal atoms, in crystals, 373
 metal oxides, 168, 169, 171
 metals, in liquid ammonia, 349
 reserve, 773
 tungstates, 369
Alkalies, spectra, 23, 24
Alkaline earth cathodes, 131, 133, 135-138
 cations, absorption spectra, 337, 338
 halides, absorption spectra, 338
Alkaloids, 407, 410, 466, 522-525, 658, 660, 726,
 791, 882, 883
Alkanes, 460
Alkyl halides, 395-401, 496
 nitrates, 352
 peroxides, 339
 radicals, 395, 398, 402
Alkylbutadiene sulfones, isomerization, 413
Alkyl-naphthylamines, azo dyes from, 626
Alkylphenylanthracenes, 509
Alkynes, and thiocyanogen, 457
Allantoin, 622
Allen-Doisy, test, 756
Allene, 415
Album cepa, 882
Alloxan, 702
Alloxazines, 852, 853
Alloy, cadmium-tin, for arc, 149, 150
Allwörden, reaction, 622
Allyl alcohol, 407, 538
 cellulose, 591
 chloride, 550
 isothiocyanate, 457
 thiourea, 863
Almond oil, 513, 743
Alopecia, 744
Alpha-particles, 35, 287, 354, 713
Alpine sunlamp, 132-135, 658, 740
Alum, in paper, 644
Alumina, 168, 171, 172, 176, 179, 350, 387, 583,
 673
 gel, 264
Aluminum, 171, 172, 359
 amalgam, 401
 and fatty acids, 554
 corrosion, 661
 electrodes, 156, 157, 159
 in carbon arc, 55, 57, 59
 lines, 190, 239
 reflector, 147
 sols, 386
 spark, 38, 153-155, 292, 299
Aluminum carbonate, 869
 chloride, 410, 411, 532, 545, 817
 hydroxide, 390, 391, 869
 phosphate, 172
 resinate, 619
 soaps, 586
Alveolar carbon dioxide tension, 753, 754
Amalgams, 149, 150, 360
Amboceptors, 759
Ames, Iowa, solar radiation at, 202
Amide ion, 349
Amides, 349, 350, 438, 458
Amines, 458, 648
 and chlorophyll bleaching, 871
 and oxidation of dye leucobases, 627
 aromatic, 495-499, 501
 as fluorescence quenchers, 262
 as polymerization inhibitors, 410
 formation from malachite green, 869
 N-substituted, 496, 497
 sensitized oxidation, 458, 863
Aminoacetanilide, 497

- Aminoacetophenone, 498
 Amino-acids, 350, 411, 670-673, 882, 883
 Aminoanthraquinones, 617
 Aminoaryldisulfoxides, 493
 Aminobenzaldehyde, 498
 Aminobenzoic acids, 498, 500, 743
 Aminodimethylaniline, 497
 Aminodiphenylamine, 624
 Aminoethylenes, 407
 Aminofluorene, 511
 Aminomethylenecamphor, 515
 Aminonaphthalene sulfonic acids, 562
 Aminonaphthol, 647
 Aminonaphtholcarboxylic acids, diazo compounds, 648
 Aminonaphtholsulfonic acids, 624, 646
 1-Amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol, 501
 Aminophenols, 468, 469, 479, 496, 497, 500, 610, 648
 Aminopiperidinobenzoyl-II-acid, 647
 Aminopyridines, 519, 520
 Amino radical, 304, 309, 319-321
 Aminostilbenesulfonic acid, 624
 Aminothiazole, 498
 Ammonia, 187, 359, 523, 647, 650, 883
 absorption spectrum, 224, 317, 349, 458
 and chloroform chlorination, 533
 and irradiated cholesterol, 793
 and unsaturated compounds, 407, 455
 as photosensitizer, 259, 303, 304, 408
 deutero, 322
 dissociation, 303, 309
 fluorescence, 258, 317, 322
 formation, 318, 353, 358, 364, 457, 458, 469, 498, 511, 672-674, 676, 689, 863
 inhibitor of chloroform oxidation, 314
 liberation, 671, 684, 702, 703, 858
 nitrogen and textiles, 621, 623
 oxidation, 193, 259, 322, 350, 883
 photolysis, 194, 211, 259, 318-322, 349
 predissociation, 241, 317, 319-321
 reaction with carbon monoxide, 322, 458
 reaction with deuterium, 320
 salts, 172, 350, 351
 silver chloride complex, 349
 Ammonium acetate, 438, 440
 azide, 323
 benzoate, 438
 carbonate, 176, 350
 chloride, 329, 350, 681
 chromate, 364
 citrate, 682
 cyanate, 459
 dichromate, 645
 hydroxide, 438, 471, 883
 molybdate, 363, 369
 nitrate, 176, 322, 883
 nitrite, 322, 351
 oxalate, 172, 444, 445, 631
 phosphates, 172, 176
 sulfate, 184, 350
 tartrate, 172
 thiocyanate, 347, 358
 Amoebae, 716, 717
Amphileptus clafaredi, microirradiation, 713
 Amygdalin, 436
 Amyl acetate, 531, 562
 alcohol, 404, 407, 462, 471, 526
 amine, 863
 nitrite, 205
 Amylase, 681, 683, 756
 Amylene, 407, 538
 Amylopectin, 436
 Analysis, fluorescence, 178, 663-665
 spectrographic, 662
 Anaphylactic shock, 748, 757, 758
 Anemias, 747, 748, 750, 774, 777
 Anesthesia, by irradiated alcohols, 402
 Angioma serpiginosum, 769
 Angstrom unit, 5
 Anharmonic oscillators, 234, 235
 Anhydro-sugars, 869
 Anilides, 455
 Aniline, 464, 469, 495-498
 aminodimethyl, 497
 black, 469, 495, 646
 benzoyl, 496
 diazo-compound, 500
 dimethyl, 497, 643
 dyes, 469, 643
 ethoxy derivatives, 498
 formation, 496, 673
 -furfural resins, 585
 green, 634
 hydrochloride, 519, 645, 646
 inhibitor of hydrogen peroxide photolysis, 340
 isodiazotate solution, 646, 647
 methoxy, 497, 498
 nitro, 495
 nitrodimethyl, 479
 nitrosodimethyl, 495, 497
 reactions, 438, 455, 456, 496
 salts of nitronaphthalenesulfonic acid, 646
 Anilinoacetic acid, 682
 Anils, phototropy, 481
 Anions, absorption by, 337, 338
 organic, electron-affinity spectra, 438
 Anisalacetophenone, 478
 Anisaldehyde, 494
 Anisidine, 659
 Anisylcinnamic acid, derivatives, 483
 Anisylidene hydrazones, 493
 Annatto, 643
 Anode, carbon, 74, 139
 glow, 30, 31
 grid for accelerating electrons, 139, 142
 ion, for mercury arc, 75
 molybdenum, 149
 processes in mercury arc, 81, 85
 thorium-layered, 156
 tungsten, 74, 78, 80
 Antagonism, of radiations, 150, 744
 Anthocyanins, 715, 890
 Anthoxyl radical, 507
 Anthracene, 382, 503-505, 511, 562, 592
 absorption spectrum, 503
 9-alkyl-10-phenyl, 509
 diaryl, 508, 510
 diradical, 505
 ethyl, 509
 fluorescence, 261, 262, 504
 in therapy, 862
 -like compounds, 468, 507
 methyl, 505, 509
 oil, 618
 oxidation, 508
 phenyl derivatives, 508
 polymerization, 205, 206, 253, 504, 505
 tolyl derivatives, 508
 Yellow, 616
 Anthranol, 508
 Anthrahydroquinol- α carboxylic lactones, 507
 Anthrahydroquinones, 507
 Anthranilic acid, 672, 673
 and cotton, 617
 Anthraquinones, and derivatives, 467-469, 474, 506, 507, 518, 521, 550
 and rubber oxidation, 603
 in therapy, 862
 Anthrax bacillus, 692, 696, 706
 Anthrone derivatives, 506, 508
 Antibodies, 757-759, 825
 Antigen-antibody reaction in skin, 742
 Antigens, 758
 Antimonious acids, 390
 Antimony, 172
 Antimony chlorides, 355, 359, 539, 545, 817, 853-855
 halides in polymerizations, 411
 lamp, 148
 oxide, 167, 168, 359
 sulfide, 389-391, 610
 tartrate, 359
 triphenyl, 592
 Antioxidants, 262, 548, 593-596, 600, 602, 603, 608, 621
 Antisera, 691, 704, 756
 Antisheep hemolysins, 758

- Antithrombin, 825
 Antitryptic activity, of serum, 757
 Antityphoid substance, 757
 Antiurease, 684
 Apomorphine hydrochloride, 522, 726
 Apozymase, 686
 Apparatus, for dye testing, 638, 640
 for irradiating liquids, 650
 for irradiating liquids, 184, 185, 829, 833
 for milk irradiation, 840-846
 for ozone formation, 292, 293
 for paint testing, 575, 576, 578-581, 586, 587
 for rubber testing, 605, 606
 high-frequency, 136
 Apples, 890, 891
 Applicators, for therapy, 62, 63, 770
 Arabinose, 432, 433, 883
Arbacia, 717, 764
 Arbutin, 436, 736
 Arcs, aluminum, 227
 anode function, 47
 as photochemical sources, 50
 beryllium, 50
 cadmium, 48, 147-150, 231
 carbon (see Carbon arc)
 cathode processes, 31, 32, 47, 48
 copper, 47, 48
 definition, 30
 enclosed vapor, 65-95
 for decomposing hydrocarbons, 62
 for 3650 Å., 179
 gold, 50
 iron, 46, 47, 49, 50, 102, 693
 low voltage, 190
 mercury (see Mercury arc)
 metallic, 46, 147-151
 nickel, 48, 50
 open, 46-64
 pole-effect, 50
 Pfund, 49
 rotating, 59
 silver, 58, 150, 231
 spectrographic, 49
 Sperry, 618
 starting, 46
 thallium, 48
 theory of, 46-48
 tungsten, 47, 50, 160
 underwater, 152
 zinc, 62, 231
 Arcaea, tincture, 658
 Arginine, 672, 677, 767
 Argon, 132, 136, 138, 139, 141, 143, 147, 279, 466, 583
 effects on photoreactions, 296, 321, 327, 329, 331, 332, 460, 463
 excitation, 26
 in starting mercury arc, 77
 ionization potentials, 27
 lines in S-1 sunlamp, 144
 Argyria, 744
 Arnica, 657
 Aromatic carboxylic acids, chlorination, 547
 compounds, halogenation, 542-549
 compounds, stability, 466
 Arsenic, 333, 354, 358, 387
 acid, 369
 chlorides, 545, 549, 854
 sulfide sols, 389-391
 Arsenicals, 549
 Arsenites, 390, 750
 Arsenous acid, 390, 750
 oxide, 167, 171
 Arsine, 332, 333, 359, 387
 tetrachloro, 549
 Artificial leather, 650
 rubber, 558
 silk, 613, 620, 621
 teeth, in black light, 178
 Artura scale, 583
 Aryl amines, 495
 azides, 648
 benzimidazoles, 743
 benzothiazoles, 743
 pyrrolinoanthranolazyls, 522
 Arylideneacetones, semicarbazones, 491
 Arythmias, heart, 862
 Asbestine, 583
 Ascaridol, 659
 Ascaris eggs, 718
 Asclepias, 890
 Ascorbic acid, 710, 848, 849, 852, 867
 Asparagine, 436, 672, 682
 Aspartic acid, 671, 672
 Aspergillus, 790, 887
 Asphalts, 610, 661
 Assimilation (see Carbohydrate photosynthesis)
 Asthmas, 776, 824
 Asymmetric photosynthesis, 266, 267, 404
 Atmosphere, absorption by, 7, 191-202
 water photolysis in, 299
 Atomic number, 21
 separation, 229, 232, 234, 235
 spectra, 19-22, 25, 230
 spectra, Bohr theory, 32, 33
 Atom-molecules, 237
 Atoms, excited, 26, 27, 229, 236-238, 257
 identification, 231
 in chain reactions, 252-254
 recombination of, 213, 231, 288
 Atoxyl, 726
 Atropine, 726, 760, 761
 Aqueous humor, 762, 764
 Aucubus leaves, 715
 Auger effect, 241, 242
 Auramine, 187, 643
 Aurantia, 634
 "Autoxypolymerization," 565
 Avena seedlings, 888
 Azelaic acid, 559
 Azides, aryl, 481
 Azidopropiondimethylamide, 266
 Azidosalicylic acid, 481
 Azine dye, 497, 640
 Azobenzene, 336, 500, 603
 Azobenzene dicarboxylic acid, 498
 hydroxy, 499, 562
 Azo compounds, 499, 500
 dyes, 624-626, 630, 640, 643, 659
 Azoisopropane, 459
 Azomethane, 459, 460
 Azonaphthalene, 503
 Azonaphthol, 503
 Azorubin, 638
 Azoxyanisole, 499
 Azoxybenzene and derivatives, 469-471, 496, 499
 Azoxy-naphthalene, 493, 503
 Azoxyphenetole, 499
 Azoxytoluenes, 499
B. *coli* (see *Escherichia coli*)
 B. diphtheriae, 704
 B. enteritidis, 825
 B. leptosepticum, 776
 B. mucosus capsulatus, 696
 B. mycoides, 709
 B. paratyphosus, 696
 B. pasteurianum, 630
 B. prodigiosus, 693
 B. subtilis, 695, 696
 B. typhosus, 693, 694, 696, 698
 Bacteria, and irradiated oils, 727, 728
 and methylene blue test for milk, 762
 and nitrogen fixation in soils, 350
 antigenic properties, 706
 differentiation, 706
 extracts, as sensitizers, 861
 growth, 886
 in air, 729
 in milk, 721
 lethal irradiation, 247, 692-707, 860
 luminous, 876
 pigment formation by, 888
 purple, 881
 sublethal irradiations, 696, 697, 828
 sulfur, 518
 Bacteriolysins, 758
 Bacteriophages, 711, 712, 860
 Baicalinase, 684

- Bakelite, 183, 584, 612
 Baking, effect on vitamin D, 830
 industry, ultraviolet rays in, 722
 Balata, 594, 602, 603
 Ballast, for lamps, 141, 146
 Ballistite, 462
 Balloon fabric, 189, 608-611
 Balmer series, 20, 22, 32, 52, 156, 163
 Bamberger reaction, 470
 Banana meal, irradiated, 829
 skin, pigmentation, 891
 Bands, physical isolation, 189, 190
 Schumann-Runge, 293-295
 spectra, 52-63, 217-228
 "Barium acid stearate," 265
 Barium carbonate, 176
 fumarate, 454
 glass, 165
 ion, 377
 lines, 26
 maleate, 454
 metaphosphate, 172
 oxide, 50, 168, 169, 171
 platinocyanide, 261
 stearate, 265
 sulfate, 384, 582, 583, 605, 609, 869
 Barley, germination, 885
 Barrels, sterilization, 725
 "Baryaire" equipment, 730, 731
 Barytes, 359, 582, 583
 Basal metabolism, 744, 746
 Basic carbonate white lead, 582, 583
 Basic colors, fading, 635
 Batiste, 189
 Bauxite, 359
 Bean roots, 887
 Beef, tenderizing, 724
 Beet, 207
 Beer's law, 207, 352, 365
 Beeswax, 559, 743
 Begonia, red pigment, 715
 Belladonna, tincture, 658
 Benedict's solution, 870
 Benzal chloride, 526, 544, 545
 Benzaldehyde, 451, 472-474, 496, 511
 and indium oxide, 360
 and nitrobenzene, 470, 471
 and potassium cyanide, 480
 and pyruvic acid, 451
 and rubber gelation, 595
 condensation product with acetophenone, 490
 derivatives, 472-476, 494, 498
 formation, 467, 470, 477, 478, 481, 483, 518, 526
 in sulfite oxidation, 356
 oxidation, 255, 423, 473, 474
 phenylhydrazine, 474
 photolysis, 468, 473, 474
 Benzaldoximes, derivatives, 493, 494
 Benzalephedrine, 688
 Benzalpyruvic acid, methyl ester, 490-492
 Benzamide, 340, 438
 Benzanilide, 438, 470
 Benzanthracene, 505
 Benzanthrone, 595
 dihydro, 505
 Benzaurin, 627
 Benzene, 187, 244, 340, 407, 411, 451, 469, 478, 479
 absorption bands, 154, 155, 466, 467
 and nitrogen peroxide, 469
 and oxygen, 466
 behavior in electrodeless discharge, 36
 detection, 467, 651
 emulsions, 391
 filter, 189, 799, 829
 fluorescence, 466
 formation, 414, 458, 472
 halogenation, 527, 542-544
 homologs, 467
 nitration, 469, 470
 reaction with bromine atoms, 514
 ring, 183
 stability, 397, 466
 Benzene derivatives
 acetylchloroamino, 496, 497
 azocresol, 496
 Benzene derivatives (*Continued*)
 azonaphthylamine, 603
 azophenyl-naphthylamine, 626
 azoxy, 469-471, 496, 499
 diazonium chloride, 500
 diazonium compounds, 625
 dihydrohexabromo, 543
 dinitro, 469, 471
 diphenyl, 592
 diphenylamino, 562
 ethyl, 488, 546
 halogen substituted derivatives, 469, 474, 542-544, 546, 547
 hexahydroethyl, 473
 hydroperoxide, 468
 hydroxyazo, 496, 499
 Benzidine, 260, 339, 479, 497, 498, 573, 610, 646, 672
 Benzil, 478
 Benzil dioxime, 498
 Benzoic acid, 478
 Benzimidazole, 852
 Benzine emulsions, 391
 Benzo colors, 638
 Benzoflavine, 264
 Benzohydroxyl, 476
 Benzoic acid, 187, 344, 515, 640
 chlorination, 547
 esterification, 480
 formation, 467-470, 473, 474, 478, 481, 483, 484, 496, 506, 508, 514, 526
 photolysis, 480
 reaction with aniline, 438
 Benzoic acids, amino, 498
 chloro, 477, 500, 546, 547, 549
 diiodobenzoyl, 498
 hydroxy, 480, 500, 546
 nitroso, 472, 474, 475, 516
 trinitro, 472
 Benzoin, 478, 480
 Benzonitrile, 494
 Benzophenone, 340, 404, 430, 476-478, 480, 507
 alkyl oximes, 478
 carboxylic acid, 478
 diamino, 562
 dihydroxy, 474
 di(hydrooxymethyl), 478
 dimethoxy, 477
 dimethyl, 477, 506, 547
 dimethylchloro, 478, 547
 Benzopinacol, 430, 476-478
 Benzopurpurin, 633
 Benzopyrene, 511, 765, 865
 Benzoquinone, 469, 474, 480
 absorption spectrum, 479
 and alcohols, 404, 480
 in photooxidations, 507
 oximes, 471
 photolysis, 101
 Benzothiazole, 183
 Benzotrithloride, 526, 544, 545
 Benzoyl acetal peroxide, 473
 Benzoxazole, 183
 Benzoylacrylic acid, 491
 Benzoylaminophenol, 496
 Benzoylaniline, 496
 Benzoylcamphor, 515
 Benzoyl chloride, 401, 547-549, 834
 Benzoylchlorophenylethylene oxide, 493
 Benzoyl ethylene derivatives, 489, 493
 Benzoyl peroxides, 410, 411, 415, 612, 834
 Benzoylphenylhydroxylamine, 496
 Benzoylpyridine, 520, 521
 Benzylacetone, semicarbazone, 494
 Benzylacetophenone, semicarbazone, 494
 Benzyl alcohols, 357, 471, 472, 526
 Benzylamine, 495
 Benzylaminobenzoic acid, 743
 Benzyl benzoate, 592
 bromide, 545
 Benzylcellulose, 463, 592
 Benzyl chloride, 401, 496, 526, 544, 545
 Benzylidene derivatives, 401, 472, 490, 493, 516-518, 522
 Benzyl iodide, 399
 Benzylmethylglyoxal, 451

- Benzylphenylacetate, 478
 Benzyl stearate, 589
 Benzylpyridine, 520, 521, 646
 Bergamot oil, and sunburn, 743
 Berlin blue hydrosols, 390
 Beryllia, 171
 Beryllium carbonate, 172
 fluoride glasses, 170, 171
 phosphates, 172
 Betaines, 626, 671
 Biacetyl, 422, 427, 429-431, 440
 Bidiphenylene-ethylene, antioxidant, 603
 Bile acids, 669, 792
 as sensitizer, 861
 Bilirubin, 745
 Bios, 175
 Biphenylenethylene, polymerization, 490
 Birge-Spencer extrapolation, 235, 236
 Bismarck Brown, 639
 Bismuth, 150
 halides, 240, 411, 545
 in carbon arc, 58
 lamp, 148
 oxide, 508
 subgallate, 479
 triphenyl, 592
 Bisulfite ion, 355, 357
 Bitumen, 661, 662
 Biviny, 408, 411
 Black body radiation, 15, 16, 155
 light, filters for, 178, 179
 Blackman reaction, 875-877, 879-881
 Bleaching, of oils, 557
 solutions, 346
 Blood, bactericidal power, 757, 775, 776
 calcium, 754, 755, 774, 776, 778, 783-785, 788,
 818, 822, 823
 catalase, 685, 825
 cholesterol, 755, 773
 clotting, 746, 825, 862
 enzymes, 742, 756
 glutathione, 825
 irradiation, effects of, 703, 746-759
 lipids, 825
 phosphorus, 754, 774, 778, 779, 783-785, 788,
 818, 822
 pressure, 733, 746
 purines, 703
 serum, 683, 746, 862 (see also Serum)
 sugar, 734, 751-753, 774
 Blood (see also Erythrocytes and Leucocytes)
 Bohr theory, 17, 21-25, 32, 33
 Bond strengths, 217, 234
 Bonds, conjugated double, 406
 Bone ash, 786, 789
 calcification, 818, 822
 cultures, 818
 decalcification, 819
Bonnemasonia asperagoides, 713
 Borax, 166, 171, 640
 Boric acid, 172, 648
 Borneol, 514
 Bornyl chloride, 550
 Boron, 64, 142
 halides, 64, 411
 hydrides, 359
 nitride, 139
 oxide, 75, 168, 169, 171, 176, 179
Botrytis cinerea spores, 696
 Bottles, and stability of contents, 343, 346
 Brackett series, 20
 Bread, irradiation, 723, 830
 "Bredig sols, 388
 "Brepheos," 175
 Breweries, use of ultraviolet rays in, 720
 Brilliant Copper Blue, 633
 Green, 259, 264, 498, 627
 Safranine, 634
 Broadcloth, 616
 Bromaniline, isodiazotate, 646
 Bromates, 348, 617
 Bromic acid, 455
 Bromides, 341
 Bromine, 211, 214, 256, 345, 359, 540-546, 548-
 550, 760
 absorption spectrum, 181, 237, 249, 275,
 345
 and carbon monoxide, 316
 and cinnamic aldehyde, 487
 and *cis-trans* conversions, 454-456
 and coumarin, 488
 and eleostearic acid, 565
 and diiodoethylene, 536
 and phenyl cinnamionitrile, 485
 and sulfur dioxide, 332
 as sensitizer, 307, 341, 485, 491, 535, 536
 atoms, 279, 280, 454, 455, 486, 537, 541, 544,
 545
 Budde effect, 283
 excitation potential, 239, 373
 induced predissociation, 243
 Bromodimethoxybenzoylacrylic acid, methyl ester,
 491
 Bromoethylbenzene, 546
 Bromoethylbromomalonate, 542
 Bromohydrocinnamic acid, 548
 Bromomethoxybutyric acids, 541
 Bromomethoxycinnamic acid, 487
 Bromomethoxyhydroxybenzaldehyde, 494
 Bromomethyl methylbenzoylbromides, 547
 Bromonaphthoquinone, 502
 Bromopentanes, 413
 Bromophosgene, 316, 317, 346, 401
 Bromosalicylaldehyde, 481
 Bromosuccinic acid, 452
 Bromotrichloromethane, 532, 533
 Bromovinylacetylene, 415
 Bronner's acid, 382
 Brownian movement, 675
 Brown-Picce sarcoma, 766
Brucella abortus, 706
Bruchus obtectus larvae, 718
 Brush discharge, 284
 Buckwheat, 745, 861
 Budde effect, 273, 282, 283
 Bunsen-Roscoe law, 205, 474, 697, 698, 714, 767
 Budick air-cooled lamp, 728
 Burns, treatment, 770
 Butadiene, 408, 411, 596
 dicarboxylic acid derivatives, 493
 dimethyl, 502, 594
 Butane, 258, 393, 394, 396, 429, 526, 531
 diiodo, 537
 diols, 833
 iso, 526, 531
 Butene, 514, 536
 Butoxybutadiene, 408
 Butter, 556, 559, 560, 562, 563, 721, 817, 831,
 835, 836, 854, 855
 Butyl alcohols, 402, 403, 538
 bromide, tertiary, 399, 464
 butadiene sulfone, 413
 chloride, 531, 657
 iodide, 396, 397
 magnesium chloride, 464
 oleate, 589
 oxide, 657
 radicals, 429
 tartrate, 657
 Butylene, 396
 Butyraldehyde, 403, 421, 422
 Butyric acid, 441, 477, 478, 540, 541, 710, 711,
 727
 dihydroxy, 407
 Butyrolin, 451
 Butyronitrile, 791

Cabbage, 689, 789, 830, 889
Cabomba caroliniana, 881
 Cacao bean sterols, 831
 butter, 556, 817
 oil, 556
 Cade oil, 513
 Cadmium, and lithopone blackening, 385
 arc, 147-150, 231, 693
 as photosensitizer, 258
 halides, 240
 heat of dissociation, 234
 lines, 5, 150

- Cadmium, oxide, 630
 - photoelectric cell, 97, 99
 - sols, 386, 387
 - spark, 167, 259, 390
- Caesium, 131, 238, 349
 - iodide, 238, 342, 372, 373
- Caffeine, 370, 522, 676
- Calanus fumarchius* respiration, 767
- Calceiferol, 806-809, 820, 821, 831
- Calcification, 778, 779, 784, 785, 818, 822
- Calcium, absorption, 745, 784-786, 818
 - and muscle, 760
 - dietary, 786, 820, 822, 824
 - excretion, 818
 - in blood, 754, 774, 776, 778, 779, 783-785, 788, 818, 822
 - in carbon arc, 57
 - in irradiated protozoa, 716
 - in plants, 888, 889
 - ions, 674, 682, 761
 - lines, 26
 - of skin, 742
 - retention coefficient, 784, 786, 830
 - salts, 763, 776
- Calcium carbonate, 176, 583, 831, 869
 - chloride, 184, 532, 704, 755, 763
 - fluoride, 52, 57, 141, 168, 172, 349
 - fructose monophosphate, 683
 - glycerophosphate, 683
 - hydroxide, 410
 - lactate, 448, 540
 - molybdate, 142
 - oxide, cathodes, 131-133, 135, 136, 138
 - oxyfluoride, 208, 349
 - phosphates, 172, 359
 - soaps, 586
 - stearate, 410
 - sucrose phosphate, 683
 - sulfate, 582, 640
 - tungstate, 142
- Calibration, of photocells, 99
 - of thermopiles, 96
 - of ultraviolet meters, 100
- Calico, 499, 616, 617, 633
- "Callophane," 664
- Calomel, 366, 367, 371, 444, 562
- Calves, rickets, 786
- Camomile, 657
- Camphane, 550
- Campholic acid, 515
- Camphor derivatives, 268, 515, 516
- Canaries, oxygen consumption by, 744
- Cancers, 511, 766
- Candlenut oil, 574
- Cane sugar, inversion, 249, 390
- Caouprene bromide, 409, 410
- Caoutchouc, 608
- Capelin, 790
- Capillaries, dilatation, 748
- Capri Blue, 264, 498
- Caproic acid, 395
- Capsicum, tincture, 658
- Carbalkoxyaryllindones, 453
- Carbamide (see Urea)
- Carbazole, 382, 504
- Carbocyanines, 381
- Carbohydrates, 431-436, 559, 695, 751-753
 - absorption spectra, 670
 - and nitrate reduction, 354
 - photosynthesis, 259, 368, 866-882
- Carbon, active, 508
 - arc, actinometry, 104
 - barium oxide in, 50
 - biological effects of, 693, 733, 747, 748, 783, 784, 889
 - carbides, in, 58
 - cerium-cored, 54, 55
 - disinfection by, 692
 - Eveready, 60-62, 576
 - flaming, 54, 527-529, 534, 578, 579, 581
 - igniting gas mixtures, 291
 - in therapy, 55-58, 62, 63, 771, 779, 836
 - industrial, uses, 59, 60, 64, 579-581, 607, 618, 640-643, 645, 653, 723, 829, 832
 - milk irradiating equipment, 842, 843
- Carbon, arc, operation, theory of, 46, 47, 50, 51, 53, 59
 - spectral energy distribution, 51, 53-56, 58, 61, 157
 - underwater operation, 64
 - with electrolyte, 59
 - with filters, 61
 - with hydrocarbons, 60
- Carbon black, 600, 609, 610
 - electrodes, 150
 - in discharge tube, 141
 - ionization potentials, 27
 - isotopes, 227
 - spark, 154
 - spectral lines, 7, 42
- Carbon dioxide, 144, 279, 343, 345, 393, 416, 539, 540, 883 (see also Carbohydrate photosynthesis)
 - absorption by, 194, 307
 - and dyes, 633
 - and linen, 615
 - and pheophorbide, 879
 - and rubber, 601
 - and smokeless powder, 462
 - conversion to formaldehyde, 194, 868, 869
 - dissociation, 240, 307
 - effects on various photoreactions, 273, 296, 298, 308, 316, 327, 329, 361, 364, 428, 469
 - formation, 64, 304, 310, 350, 394, 400, 403, 422, 425, 431-433, 437-442, 445, 447-452, 454, 456, 457, 461, 462, 469, 470, 477, 478, 480, 511, 514, 515, 518, 521, 614, 615, 626, 673, 674, 739, 863
 - in accelerated tests, 580, 590
 - in fermentation, 709
 - in gasoline testing, 653, 654
 - in milk sterilization, 722
 - nascent, 870
 - photolysis, 45, 307, 308
 - photoreaction with hydrogen, 308
 - reduction, mercury-sensitized, 258
- Carbon disulfide, 62, 64, 354, 391, 463, 510, 833
 - monosulfide, 354
 - monoxide, 370, 393, 652
 - absent near carbon arc, 51
 - absorption spectrum, 308, 687
 - adsorption on quartz, 309
 - and dyes, 633
 - and fermentation, 710, 711
 - and fluorine, 317
 - and peroxidase, 686
 - and plant photosynthesis, 876
 - catalase compound, 685
 - conversion to formaldehyde, 72
 - effects on various photolyses, 296, 316, 322
 - ferrocystein compound, 687
 - ferroglutathione compound, 687
 - filter, 309
 - formation, 64, 307, 333, 334, 394, 395, 399, 402, 405, 416-418, 420-422, 424-434, 448, 449, 460-462, 465, 472, 473, 478, 521, 614, 671
 - heat of dissociation, 235, 308
 - hemin compound, 687
 - hemoglobin, 687, 688, 749
 - indophenoloxidase compound, 686
 - in mercury-sensitized water formation, 310
 - in oxidation of nitrogen, 324
 - in silent discharge, 310
 - ion, 237
 - iron-porphyrin compounds, 687
 - oxidation, 250, 304, 308-313, 315
 - photolysis, 308
 - poisoning, 749
 - reaction with amines, 322
 - reaction with ammonia, 322, 458
 - reaction with bromine, 316
 - reaction with chlorine, 310-314
 - reaction with ClO radicals, 312
 - reaction with hydrogen, 310
 - reaction with methanol, 439
 - reaction with nitric oxide, 310
 - Warburg enzyme compound, 687
- Carbon suboxide, 308, 447
- Carbon subsulfide, 62, 64

- Carbon tetrabromide, 345, 395, 401
 Carbon tetrachloride, 182, 279, 359, 409, 526-528
 absorption spectrum, 395, 396
 and bromine oxide, 346
 formation, 532, 533
 in rubber cements, 597
 photoreactions of, 354, 400, 529
 Carbons, *see* 51, 64
 Carbonyl chloride, 539 (*see* Phosgene)
 Carbonyl group, 416, 425, 426, 437
 Carbonyl hypohalides, 440
 Carbostyryl, tetramethoxyphenyl, 484
 Carboxy-acids, 467, 547
 Carboxyl radical, 540
 Carcinogenic agents, 765, 865
 Carcinomas, 755, 766
 Carmine II, 634
 Carnauba wax, 410, 608
 Carotene, 512, 555, 856, 871-873, 876, 882
 absorption spectrum, 853, 854
 and burns, 740
 and fermentation, 710
 and visual purple, 858
 as sensitizer, 862
 bleaching, 854, 856, 871
 conversion into vitamin A, 854
 formation, 888
 Carrots, destruction of vitamin A, 856
 Carvacrol, 513
 Carvone, 515
 Caryophylline nitrosite, 515
 Casein, 583, 620, 674, 678
 Cassia oil, 513
 Castor oil, 411, 557, 559, 562, 574, 591, 612, 683
 Catalase, 560, 680, 685, 742, 756, 825, 874, 877, 889, 890
 Catalysts, 253, 254, 444, 498, 531, 532, 539
 Cataplasma, 657
 Cataracts, 763
 Catechin, 479
 Catechol tannin, 651
 Catechu, 613
 Cathode rays, 35, 152, 156, 657, 804, 828, 832
 Cathodes, nickel, 160, 161
 nickel oxide, 132
 oxide-coated, 131-133, 135, 136, 138-140, 146, 151, 152, 160
 Schüler, 151
 sputtering, 139
 tungsten, 131, 161
 Wehnelt, 76, 131, 133, 156
 Cattle, irradiation, 835
 Celanese, 188, 643
 Cell absorption, 270, 271
 Celloidin, 463
 Cellophane, 185, 325
 Cells, filter, 184
 photoelectric, 97, 99, 100, 107
 photronic, 96, 97
 Celluloid, 9, 167, 407, 462, 463, 592
 Celluloid-like products, 411
 Cellulose, 562, 617, 618, 626
 acetate, 173, 463, 585, 588, 591, 640
 acetate silk, 188, 616
 acetobutyrate, 411
 and dyes, 633
 and flavanthrene, 635
 benzyl, 463
 derivatives, 589, 621
 deterioration, 613-617
 ester, 173, 621, 648
 ethers, 648
 ethyl, 463, 591
 hydrate, 167, 562
 lacquer, 51, 588
 nitrate, 462, 585, 591, 618
 regenerated, 173, 562
 trichloronate, 621
 "Cel-O-Glass," 170, 174, 175, 782
 Cephalin, 669
 Cereals, irradiation, 722, 789, 827, 829, 830
 Ceresin, 610, 661
 Cerevisterol, 792
 Cerium, 23, 54, 97, 98, 174, 592
 fluoride, 51
 hydroxide, 390, 432, 450
 nitrate, 166
 oxide, 165-167
 perchlorate, 370
 peroxide, 573
Chaetopterus eggs, 764
 Chain reactions, 213-215, 249, 252-255, 259, 356, 357, 497
 bromination of acetylene, 537
 bromination of cinnamic acid, 486
 chlorinations, 532, 535, 542, 543
 hydrogen-chlorine combination, 283-285, 287-290
 hydrogen-oxygen combination, 301, 302
 hydrogen peroxide photolysis, 340
 iodine-sensitized ethylene iodide photolysis, 536
 ozone photolysis, 297, 298
 styrene polymerization, 489
 Chalcone and derivatives, 490, 491
 Chalking, of paints, 577, 578, 581, 583, 589
 Chalks, 575, 582
 Charcoal, 171, 226, 341, 392, 469
 Chardonnet silk, 188
 Charges, electric, removing from paper rolls, 662
 Checking, of paints, 577-579, 590, 603, 606, 607
 Cheese, 563
 Chemoluminescence, 265, 464, 878
 Cherry-laurel water, 456
 Chicago, antirachitic radiations at, 170, 173
 Chicken food, antirachitic, 834
 Chickenpox, 775
 Chicks, and hay extract, 790
 encephalomalacia factor, 856
 irradiation, 787, 788
 leg weakness, 175, 202, 787
 phosphatase, 819
 rickets, 143, 781, 782, 813, 817, 837
 China clay, 583
 Chinawood oil, 564-567
Chlamydomonas eugametos, gametes, 767
 Chloral hydrate, 416
 Chloramine, 105, 721
 Chlorantin colors, 644
 Chlorates, 307, 346, 348, 349, 617
 Chlorazol dyes, 616, 633, 638, 642
Chlorella, 713, 714, 874-877, 882, 883
 Chlorotone, 717
 Chlorhexane, 530
 Chloric acid, 298, 346, 548
 Chloride excretion, 760
 Chlorides, 341, 343, 346, 348, 384, 439, 751
 Chlorinated olefines, as solvents, 534
 Chlorinated rubber, 611, 612
 Chlorination catalysts, 531, 532, 539
 Chlorinations (*see* the compounds chlorinated)
 Chlorine, 187, 211, 215, 256, 291, 359, 400, 527-529, 531, 542, 543, 546, 547, 549, 550, 721, 760
 absorption spectrum, 181, 235, 237, 244, 249, 281, 282, 291
 and copper, 359
 and hydrogen atoms, 540
 and natural gas, 526-528
 as sensitizer, 259, 297, 298, 302, 303, 310, 314, 318
 attempted activation of, 284
 atom, 302, 306, 529, 532-535, 540
 reactions of, 213, 283, 284, 306, 313-316, 348, 540
 bleaching, 617, 618
 carrier, 544
 dissociation, 237, 282, 283, 287, 291, 311, 312, 314
 excited molecules, 269, 287, 290, 291, 311
 filters, 181, 182, 314, 800
 formation, 305-307, 347, 348, 361, 400, 451, 506, 546
 in milk sterilization, 722
 isotopes, 227
 of skin, 742
 photoexpansion, 282, 284, 285
 reaction with COCl_2 molecule, 312, 313, 315
 reaction with formaldehyde, 418
 reaction with sulfur chloride, 355
 reaction with sulfur dioxide, 331, 332
 triatomic, 284, 288, 302, 311, 313
 water, 205, 346, 614

- Chlorine dioxide, 243, 285, 306, 307, 347, 348
 heptoxide, 348
 hexoxide, 298, 307, 348
 monoxide, 305-307, 347, 348
 Chlorites, 346
 Chloroaminopyridine, 520
 Chloroanthraquinones, 506, 507, 617
 Chloranthrone, 508
 Chlorobenzene derivatives, 543, 544, 546, 547
 Chlorobenzoic acids, 477, 500, 546
 Chlorobenzophenone, 477
 Chlorobromobenzene hexachloride, 544
 Chlorobromomethylbenzene, 546
 Chlorocineole, 550
 Chlorocinnamic acid, 483
 Chlorocumene, 550
 Chlorocyclohexene, 543
 Chlorodibenzoylethylene, 489
 Chloroethyl ether, 546
 Chloroform, 528
 absorption and photolysis, 396, 400
 action of x-rays on, 209
 and quinine, 523
 chlorination, 532, 533
 formation, 452
 oxidation, 314, 532
 photolysis, 529, 400
 Chloroformic acid, 539
 Chlorohydroxyanthraquinone, 507
 Chloriodoethylene, 412
 Chloromethoxybenzaldehyde, 494
 Chloromethoxybenzophenone, 477
 Chloronaphthalene, 549, 592
 Chloronaphthoquinone, 502
 Chloronitrodiaminotriphenylmethane, 626
 Chloronitrosocyclohexane, 461
 Chloronitrosophenol, 479
 Chloroolefines, 531
 Chlorophyll, 260, 261, 263, 264, 555, 791, 871, 888
 absorption bands, 870, 871
 and hydrogen, 679, 680
 absence of photoelectric effect, 872
 bleaching, 871, 872
 -carbon dioxide compound, 871, 875-877, 880
 chemoluminescent glow, 864
 diradical, 510
 fluorescence, 864, 877, 878
 formation, 886-888, 890
 green, 611
 orientation in chloroplast, 881
 peroxide, 863, 872
 photoactivity, 872
 photolysis, 680, 871
 photooxidation, 863, 871, 872, 878
 relation to carbohydrate photosynthesis, 862, 866, 872, 873, 877
 sensitizer, 434, 451, 490, 498, 522, 553, 560, 625, 626, 678, 749, 860, 862, 864
 skin sensitization by, 741
 -water complex, 877
 Chlorophyllase, 873
 Chlorophyllin, 872
 4-Chloropicolinic acid, 520
 Chloropicrin, 460
 Chloroplasts, 715, 866, 871, 881
 Chloroprene, polymerization, 596
 Chloropropanes, 526, 531
 1-Chlorosuccinic acid, 452
 Chlorotoluenes, 544, 549
 1-Chlorovinylacetylene, polymerization, 415
 "Chlorozone," 288
 Chocolate, irradiated, 831
 Choke, for starting mercury arc, 92
 β -Choladienic acid, 817
 Cholic acid, 817
 α -Cholatrienic acid, 817
 Cholehamatin, as photosensitizer, 861
 Cholera phage, 712
 vibrio, 706, 758
 Cholestadiene, 817
 Cholestantriol, 792
 Cholesterol, 660, 756, 793, 812, 818
 absorption spectrum, 794
 antrachitic activation, 791-793, 795, 796, 802-804
 Cholesterol, contaminants as provitamins, 813-816, 834
 7-dehydro, 794, 811, 815-817, 834
 dielectric constant, 794
 dihydro, 791, 794
 esters, 792
 fluorescence, 735
 in blood, 755, 773, 825
 in skin lesions, 742, 766
 irradiated, skin absorption, 847
 of wool, 623
 oxidation, 559
 soles, 669
 Cholesterolized antigen, 758
 Cholesteryl oxides, 792
 Cholic acid, 670
 Choline, 669, 677
 Christiansen filters, 189
 Chromates, 364
 Chrome Green, 615, 633
 pigments, 582
 Chromic acid, 206, 209, 251, 252, 364, 450, 524, 525
 hydroxide, 389, 404, 469
 sulfate, 439
 Chromium, 167-169
 cations, 337
 chromate, 404
 coatings for arc carbons, 51
 complex salts, 363, 369
 hydroxide, 615, 633
 in cored carbon arc, 57
 lines, 26
 mirror in discharge lamp, 139, 142
 reflectors, 147
 salts, 187, 359, 443, 617
 trioxide green, 612
 Chromophore theories, 624
 Chromoprotein, in algae, 881
 Chromosomes, 703, 704, 718
 Chromotrope-2R, 260
 Chromyl chloride, 365
 Chrysis, 744
 Chrysogen, 504, 511
 Chrysoidine, 616
 Ciba Blue, 616
 Cibanone colors, 161, 616, 633
 Cinchonidine, 524, 658
 Cinchonine, 524, 525
 Cinchoninic acid, 508
 Cineole, 550
 Cinnabar, 367
 Cinnamaldehyde, 423, 474, 482, 484, 487
 nitro, 475
 semicarbazone, 494
 Cinnamalmalonic acid, dimers, 485
 Cinnamanilide, 484
 Cinnamic acids, 185, 482-487, 490, 491
 and nitrobenzene, 470, 471
 formation, 474, 482
 halogenation, 255, 267, 485-487, 547
 Cinnamic anhydride, 484
 Cinnamide, 484
 Cinnamon oil, 513
 Cinnamitrile, α -phenyl, 743
 Cinnamylideneacetic acid, 484, 485
 Cinnamylideneacetophenone, 485
 Cinnamylidene-*m*-nitroacetophenone, 485
 Circuits, electrical, for spark production, 39-42
 for starting mercury arc, 76, 77
 for underwater spark, 154
 Circulatory system, and irradiation, 733, 746
Cis and *trans* compounds, absorption spectra, 412, 413
 interconversions, 457
 Citraconic acid, 456
 Citraconic anhydride, 806, 807, 834
 Citral, 513
 Citric acid, 369, 377, 648
 and ferric iron, 361, 362
 and pyridine, 518
 bromination, 540
 in tobacco, 884
 oxidation, 364, 448, 450
 reduction of stannic acid, 366

- Citric acid, ultraviolet sensitizer for plates, 381
 uranium-sensitized photolysis, 450
 Clark lithopone units, 716
 Clay, in rubber, 610
 Cleveland, solar energy at, 196
 Cloth, 188, 189, 727
 Clouds, effect on solar radiations, 198, 201
 Clove oil, 513
 Cluster theory, Weigert, 285
 Coagulation time, blood, 746
 Coal-tar, 512, 600, 865
 Cobalt, 166, 167
 and lithopone blackening, 385
 cations, 337
 complex salts, 260, 368, 444, 445, 479
 drier, 572, 574, 592, 596
 glasses, 165, 168
 hydroxide, 368
 in carbon arc, 57
 lines, 26
 oxide, 165, 179
 salts, 187, 188, 359, 367-369, 403, 409, 444, 591,
 596, 869, 870
 sulfate filter, 347
 Cobra venom, 691
 Cocaine, 268, 522, 658, 726
 Cocoa, fluorescence, 556
 Coconut oil, oxidation, 559
 Codeine, 525, 726
 Cod-liver oil, absorption spectrum, 555
 and calcium metabolism, 784, 785, 818
 and rickets, 779, 780, 786, 788, 813-815
 conductivity, 556
 irradiated, 728, 789, 791, 831
 oxidation, 559
 Cod-liver oil, toxicity, 822
 vitamins, 780, 793, 820, 834, 838, 854, 855
 Coenzymes, 680, 686-688
 Coffee, 660
 Coil, inductance, for starting mercury arc, 77
 induction, 136, 148, 149, 152
 preheating for starting mercury arc, 76
 Tesla, 153
 Colds, and ultraviolet irradiations, 775, 776
 Coleus, 886
 Collagen, fluorescence, 651
Colletotrichum phomoides, 711
 Collidine, 519
 Collisions, deactivating, 215, 231, 335
 of first kind, 257
 of second kind, 257, 258, 261, 262
 Collodion, 177, 462, 463, 479, 588, 627, 632
 Colloidal systems, 64, 386-392
Collybia dryophila, 711
 Color centers, in crystals, 373-375
 Color photography, 627
Colpidium, sensitive molecules, 696
 Coltsfoot, 657
 Colza oil, 559, 612
 Combustion, and ultraviolet rays, 652
 Complement, 757-759
 Complex radiations, summed effects, 255, 256, 441
 Condensers, in production of sparks, 40-42, 153
 Cones, of retina, 857
 Congo Brown, 639
 Red, 389, 625, 633
 resin, 585
 Coniferin, 436
 Conjunctivitis, 164, 763
 Conquinine sulfate, 521
 Constant, Planck's, 8
 solar, 1
 Cooper-Hewitt arc, (see Mercury arc)
 Copal, 591, 610
 Copper, 258, 359, 415, 442, 463, 546
 ammonia complex, 179, 188
 and chlorine, 359
 and ergosterol, 832
 and fatty acids, 554
 and methylene blue-alcohol dehydrogenase, 686
 arc, 47, 48
 compounds and benzylcellulose films, 592
 catalyst, 469
 cation, 337, 377
 cells, in actinometry, 105
 egg white sensitizer, 553
 in carbon arc, 57
 irradiated, 748
 line, 240
 number, 614, 616, 618-620, 633
 oxidation, 359
 salts, 184, 187, 188, 359, 362, 409, 498, 531,
 553, 589, 603, 610, 617
 sensitizer, 265
 sols, 386, 389, 391
 underwater spark, 153, 155
 Copper arsenate, in carbohydrate photosynthesis,
 870
 carbonate, 522, 883
 hydride, 237
 hydroxide, 389, 657
 oxides, 179, 304, 442, 508, 563, 655
 soaps, 586
 sulfate, 184, 186, 187, 347, 357, 439
 Coprosterol, 792
 Corallin, 381, 629
 Coramine, 520
 Cordite, 462
 Corex (see Glass)
 Corium, of skin, 735, 736
 Corn, 886-888
 meal, bleaching by sparks, 45
 oil, 557, 574
 silage, 790
 Cornea, of eye, 164, 762
 Corneum, of skin, 735, 736, 739
 Corpuscular theory, 3
 Corrosion, of metals, 661
 Cosine law for intensity and angle of irradiated
 surface, 771
 Cosmic rays, 9
 Cotton, 188, 502, 608, 613-618, 620, 621, 626, 633,
 637, 639, 646
 fluorescence, 645, 646
 printing, 495, 498
 Cottonseed oil, 557, 558, 789, 847
 Cottonedons, 886
 Coumaric acids, conversion to coumarin, 488, 503
 Coumarin, and derivatives, 487, 488, 503, 562,
 609, 660
 Coumarone-indene resins, 585
 Counter, Geiger-Müller, 100
 Cozymase, 686, 687
 Crackers, irradiation, 830
 Cracking of paints, 577, 578
 of rubber, 606, 609
 Cragmor, solar energy at, 198-200
 Crayons, 648
 Cream, irradiation of, 841
 Creatine, excretion, 745
 Creatinine, 745, 858
 Crêpe de Chine, 188
 Crêpe rubber, 595, 598, 600, 602, 604, 605
 Cresol, 390, 469, 479, 513
 dinitro, 499
 vinyl derivatives, 411
 Cresolbenzene, 562
 Cress seedlings, 715
 Cresyl Blue, 365, 634
 Cresyl Fast Violet, 634
 Crocein, 629
 Crocetin, derivatives, 767, 856
 Crocin, 767
Crotalus terrificus toxin, 678, 691
 Crotonaldehyde, 424, 425
 Crotonic acid, 407, 455, 456, 541, 565
 Crotonic amide, 455, 456
 Crotyl cellulose, 591
 Cruxite A, 166
 Crystal Ponceau, 632
 Crystal Scarlet, 625
 Crystal Violet, 105, 627-629, 633, 634
 Crystals, absorption spectra at low temperatures,
 336
 anisotropic effects, 348, 353
 defects, and latent image, 374, 378
 diffraction of x-rays, 8
 lattice energy, 372, 378
 photoprocesses, 372-376
 Cucumber plants, 885-888
 Culture media, irradiation of, 709
 Cumene, 550

- Cumidine, 513
 Cuminylidene hydrazones, 493
 Cuprammonium rayon, 188, 613, 614, 621
 Cuprene, 414
 Cyanamide, 354
 Cyanides, 265, 878
 Cyanins, 183, 632, 634, 636
 Cyanocyclopropane, and derivatives, 542
 Cyanogen, 52, 53, 192, 218, 363, 456-458
 Cyclobutane derivatives, 484, 492
 Cycloheptanone, 429
 Cyclohexane, 182, 407, 429, 466, 473
 carboxylic acid, 547
 1-chloro-1-nitroso, 461
 halogenation, 211, 542-544
 irradiation with air, 656
 nitration, 470
 Cyclohexanol, 403
 Cyclohexanone, and derivatives, 395, 403, 429, 516, 517
 Cyclohexenes, 407, 413, 543, 547
 Cyclohexenones, 516
 Cyclohexylamine, derivatives, 612
 Cyclopentane, and derivatives, 429, 448
 Cyclopentanone, and derivatives, 429, 516
 Cyclopropane, and derivatives, 395, 447, 466, 541, 542, 546, 653
Cyclops, 684, 767
 Cylinder oil, 653
 Cysteine, 433, 463, 673, 679, 750
 Cystine, 623, 672, 673
 Cytochrome, 687
 Cytolysis, 716, 717
 Cytosine, 677, 696, 699, 701
- D**
 Dahlia, dye, 634
 Dammar, 590, 610
 Datura plants, 889
 Davos, radiation at, 195
 Decachlorocyclohexene, 543
 Decalin, 511, 657
 Decenic acid, 553
 Dehydroascorbic acid, 848
 Dehydrochlorophyll, 878, 879
 7-Dehydrocholesterol, 796
 7-Dehydrocholestenopinacone, 817
 7-Dehydrocholesterol, 794, 811, 813, 815-817, 834
 Dehydroergosterol, 810, 812
 Dehydrogenases, 686, 687, 760
 Dehydrolumisterol, 810, 812
 Dehydrorubrene, 603
 7-Dehydrositosterol, 811, 816, 817
 7-Dehydrostigmastanol, 817
 Dental caries, 824
 Dentistry, ultraviolet radiations in, 769
 Dermatitis, 772, 861
 Dermatol, 479
 Dermatology, radiations in, 769, 861
 Derris, 659
 Desensitizers, 439, 440, 863
 Designs, reproduction of, 648
 Desoxycholic acid, 817
 Deuterioflavin phosphate, 853
 Deuterium, 290, 302, 320, 332, 394, 882
 Deuterium iodide, 305, 344
 Dewar flasks, filters, 187
 Dextrins, 387, 388, 435, 436, 682
 Dextrinose, 435
 Dextrose, 183, 339, 371, 383, 883
 absorption spectrum, 431
 and anthraquinones, 507
 and diastase, 681
 and methylene blue, 630
 fermentation, 709
 photolysis, 432, 433
 reduction of tungstic acid, 387
 Diabetes, 752, 774
 Diacetone alcohol, 427
 Diacetoxyanthraquinone, 506
 Diacetoxyhelianthron, 506
 Diacetoxyanthradianthron, 506
 Diacetyl, 421
 Diacetyl-diaminodiphenylamine, 497
 Diacetylene, 415
- Diagrams, energy-level, 27-29, 92, 219, 220, 229, 232-236
 Dialdehydeazobenzene, 498
 Dialkyl-diarylfumarates, 453
 Diallyl, 594
 Diallylthiocarbamide, 871
 Diamagnetism, of crystals, 379
 Diamin Fast Yellow, 616
 Diaminoazoxytoluene, 499
 Diaminobenzophenone, 562
 Diaminonaphthalene, 497, 501
 Diaminophenazine, 497
 Dianisidine, 479
 Dianthracene, 262, 504
 Dianthraquinonylthane, 506
 Dianthraquinone, dihydroxy, 506
 Dianthrone, dimethoxy, 506
 Diarylanthracenes, 508
 Diarylmalic acids, 454
 Diastase, 680-682, 742, 752
 Diatomic molecules, energy of, 232-234, 240
 Diatoms, 790
 Diazoaminobenzene, 575
 Diazobenzenesulfonic acid, 500
 Diazocamphor, 516
 Diazo compounds, 460, 499, 500, 647, 648
 in actinometers, 105
 in textile printing, 645
 photolyses, 624, 625
 Diazo, diphenylamine sulfate, 625
 1-Diazo-2-hydroxy-3-naphthoic acid, 648
 Diazomethane, 460
 Diazonaphtholsulfonic acid, 624, 625
 Diazonium salts and textile printing, 646
 Diazo papers, 647, 648
 Diazo printing, 645, 647
 Diazo process, in photography, 384
 Diazosalicic acid, 481
 Diazosulfanilic acid, 499, 500
 Diazotized aniline, 646, 647
 Diazotypes, 647, 648
 Dibasic acids, 440-448
 Dibenzalacetone, 743
 Dibenzanthrene, 765
 Dibenzofuran, 592
 Dibenzoylbisomoethylene, 489
 Dibenzoylcyclobutane, 492
 Dibenzoyldibromoethylene, 489
 Dibenzoyldichloroethylene, 489
 Dibenzoyldimethylnaphthalene, 549
 Dibenzoyl peroxide, 480, 722, 723
 Dibenzoyl-tetraphenyltetrahydropyran, 268
 Dibenzyl ether, 405
 Dibromobenzoylbenzoic acid, 498
 Dibromoethane, 440
 Dibromoethylene, 412, 537
 Dibromoisatin, 616
 Dibromomethoxyphenylpropionic acid, 487
 Dibromopinacolone, 539
 Dibromopropane, 546
 Dibromophenylcyclopropane-1,2-dicarboxylic acid, 541
 Dibromosalicylic acid, 548
 Dibromotetrachlorethane, 401
 Dibutyl phthalate, 481, 576, 612
 Dibutyl tartrate, 173
 Dichloroacetic acid, 401
 Dichloroacetyl chloride, 401, 407
 Dichloroacetylene, 538
 Dichloroanthracene, 703
 Dichloroanthraquinone, 506
 Dichloroazobenzene, 499
 Dichlorobenzene, 543
 Dichlorobenzene, hexachloride, 543
 Dichlorobenzoic acid, 549
 1,5-Di(*o*-chlorobenzoyl)-naphthalene, 549
 Dichlorocamphane, 550
 Dichlorocinnole, 550
 Dichloroethane, 401, 526
 Dichloroethylene, 412, 413, 535, 537
 Dichlorodimethylbenzoylchloride, 548
 4,4-Dichloro-1,3-dithiacyclobutane-2-one anil, 464
 Dichlorohydrindones, 517
 Dichloromethane, 526, 532
 1,2-Dichloro-2-methylpropane, 532

- 1,2-Di(chloromethyl)2-methylpropane, 532
 Dichloromethyl sulfate, 538
 1,3-Dichloro-2-phenylpropane, 550
 Dichloropyridine aldehydes, 520
 Dichlorotoluene, 549
 Dichroism, circular, 266, 383
 Dichromates, 363-365, 384, 721
 Dichromic acid, 524
 Dicinnamalacetone, 485
 Dicyclohexylamine, 612
 Dicyclopentadiene, 538
 1,5-Di(2,5-dichlorobenzoyl)-2,6-dichloronaphthalene, 549
 2,4-Di(dichloromethyl) benzoyl chloride, 548
 Didymium, 167
 Didymium glass filter, 177, 178, 616
 Dielectric constants, 249, 253
 Diethyl-allylthiocarbamide, 631, 871
 Diethylaniline, 643
 Diethyl colludenedicarboxylate, 519
 Diethyl cyclopropane-1,1-dicarboxylate, 447
 Diethyl dibromosuccinate, 454, 455
 Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate, 526
 Diethyl diphenylfumarate, 453
 Diethyl diphenylmaleate, 453
 Diethylene dioxide, 833
 Diethyl ether (see Ether)
 Diethyl ketone, 421, 428, 595
 Diethyl maleate, 407
 Diethyl phthalate, 173
 Diethyl tartrate, 407
 Diethyl toluhydroquinone benzoate, 474
 Diffraction, 3, 4, 6-8
 Difluorenylene, 511
 Diffuse bands, 241, 243
 Diffuse series, 23, 24
 Diffusion, and temperature coefficients, 248
 Di-furoyl peroxide, 517
 Digitalis, 268, 658, 890
 Digitonin, 670, 793
 Diglycol, 405
 Diglycollic acid, 405
 Dihydrobenzanthrone, 505
 Dihydrochalcone, 490
 Dihydrocholesterol, 791, 794
 22-Dihydroergosterol, 811-813, 817, 834
 Dihydroisophthalic acid, 481
 Dihydronaphthalenes, 501
 Dihydronaphthylacetic acid, 511
 Dihydrophytosterol, 791
 Dihydrorotenone, 659
 Dihydroxyacetone, 339, 404, 428, 432
 Dihydroxyanthraquinone, 469
 Dihydroxybenzaldehyde, 498
 Dihydroxybenzophenone, 474
 Dihydroxybutyric acid, 407
 Dihydroxydianilinoinodophenol, 497
 Dihydroxydianthraquinone, 506
 Dihydroxy-dinaphthyl-diquinone, 502
 Dihydroxydiphenylpropane, 612
 9-(2,3'-Dihydroxy-1'-isopropyl)-isoalloxazine, 852
 4,4-Di(hydroxymethyl)benzophenone, 478
 Dihydroxyphenols, 833
 Dihydroxyphenylalanine, 671
 Diindyl-m-methoxy-p-hydroxybenzylidene, 517
 Diiodobenzoylbenzoic acid, 498
 Diiodobutane, 537
 Diiodoethane, 400
 Diiodoethylene, 399, 536
 Diiodomethane, 400
 Diisoxazole ketone, 517
 Diisoxazolinol, 517
 Diketones, 404, 429, 431, 478, 514
 Diketopiperazines, 674
 Diketostearic acid, 574
 Dimethoxyanthracene photooxide, 508
 Dimethoxybenzaldehyde, 494
 Dimethoxybenzanthrone, 506
 Dimethoxybenzophenone, 477
 6,7-Dimethoxy-1-benzyl-N-methyl-1,2,3,4-tetrahydroquinoline-1-carboxylic acid, 521
 Dimethoxydianthronone, 506
 Dimethoxyhelianthronone, 507
 Dimethoxynaphthadanthronone, 507
 Dimethoxyphenazine, 497, 498
 Dimethoxypyrene, 562
 Di-p-methoxystyryl ketone, 489
 Dimethylacetaldehyde, 421
 Dimethylalloxazine, 852, 853
 Dimethylaminoacetophenone, 629
 Dimethylaminobenzaldehyde, 498
 Dimethylamino-methylcoumarin, 609
 Dimethylaniline, 497, 643
 hydroxy, 497
 Dimethylantraquinone, 506
 Dimethylbenzophenone, 477, 506, 547
 Dimethylbenzoyl chloride, 547, 548
 Dimethylbutadiene, 502, 594
 Dimethyl carbonate, 539
 Dimethylchlorobenzophenone, 547
 Dimethylcoumaric acid, 503
 Dimethylcoumarin, 503
 Dimethylcyclohexenone, 516
 Dimethylcyclohexyl adipate, 650
 2,2'-Dimethyl-9,9'-dihydroxy-1,1'-dicarboxylic diacetone, 507
 bis(Dimethylbenzoyl)ethylene, 489
 Dimethyldiphenyltruxone, 517
 Dimethyl ether, 405, 459
 Dimethylethylene, 429
 Dimethyl fumarate, 453
 Dimethylhexene, 461
 Dimethyl-n-hexyldimethyl carbinol, 428
 Dimethyl maleate, 453
 Dimethylphenazine, 497
 2,3-Dimethyl-1,4,11,12-tetrahydrophenanthrenequinone-11,12-endo-2/3'-dimethyl-2'-butene, 502
 Dimethylditolyl fumarate, 453
 Dimethylditolyl maleate, 453
 Dinaphthalene azotide, 497
 Dinaphthazine, 497
 Dinaphthylanthracenes, 508
 Dinitroazoxybenzene, 499
 Dinitrobenzaldehyde, 475
 Dinitrobenzene, 469, 471
 Dinitrobenzoyl chloride, 834
 Di-nitrobenzylidenetrierythritol, 472
 2,5'-Dinitro-5,5'-dimethoxydiphenyl disulfide, 500
 Dinitronaphthalenesulfonic acid, 501
 Dinitrophenol, 499
 Dinitrotrammine cobalt, 368
 Dinitrotoluene, 470-472
 Dinitrotriphenylmethane, 626
 Dinitrosohydroxybenzyl alcohol, 471, 472
 Dioxytriphenylanthracene, 511
 Diparatungstic acid, 369
 Dipptides, 674
 Dipentene-3-methane, 514
 Diphenosuccindan-9,12-dione, 550
 Diphenyl, 480
 Diphenylacetyldiphenylmethane, 493
 Diphenylallyl ether, 493
 Diphenylamine, 462, 591
 Diphenylaminobenzene, 562
 Diphenylanthracene, 508, 510
 Diphenyl-4,4-bis-(8-azo-N-phenyl-β-naphthylamine), 626
 Diphenylbenzene, 592
 Diphenylbenzopinacol, 477
 Diphenylcyclobutane-2,4-diatroponitrile, 484
 Diphenacyldiphenylmethane, 521
 Diphenylene ethylene, 408
 Diphenylethane, 478
 Diphenyldimethyltruxones, 492, 493, 517
 Diphenyl-bis-diphenylethane, 626
 Diphenyl-di-2-pyridylethane, 520
 Diphenylfuran, 498
 Diphenylglyoxime, 461
 Diphenylguanidine, 592, 605, 610, 612
 Diphenyl ketone, 595
 Diphenylmethane dyes, 640
 Diphenylnaphthacene, 510
 2,3-Diphenyl-α-β-naphth-1,2,3-triazolium picrate, 626
 1,3-Diphenyl-2,4-bis-(β-phenyl-β-cyanovinyl) cyclobutane, 484
 Diphenyltruxone, 493, 517
 Diphsogene, 539
 Diphteria, 825
 bacillus, 704

- Diphtheria, toxin, 690, 691
 Dipropylglycol, 403
 Dipropyl ketone, 429
 Diradical, rubrene, 509
 Direct dyes, 616, 635, 642
 Direct Scarlet, 390
 Diricinoleic acid, 554
 Disaccharides, 434
 Discharge, electrical, classification, 30, 32
 electrodeless, 36, 37, 157
 glow (see Glow discharge)
 hydrogen (see Hydrogen, discharge)
 mercury (see Mercury, discharge lamps)
 silent, 292, 310
 Disilane, 333
 Displacement law, Wien, 94
 Dissociation, 212, 214, 216, 218, 227, 229-244
 Distyryl ketone, 489
 Disulfides, 463
 Distemper, 777
 Ditetrahydrofurfurylamine, 612
 1,2,7,8-Di-(1,5-tetrazo)-4-methyl-(1,8-naphthyl-
 dine, 1,2,7,8-tetrahydride), 503
 Dithiocyanohethanes, 457
 Dithiocyanethylene, 457
 Dithionate ion, 355, 356
 Di-*o*-tolylguanidine, 605
 2,4-Di(trichloromethyl)benzoyl chloride, 548
 Diuresis, 760
 Divinylacetylene, 415
 Dodecachlorocyclohexane, 543
 Dodecylaldehyde, 424
 Doebner's violet, 629
 Doppler effect, 231
 Dogfish oil, 833
 Dogs, 745, 786
 Dopa, formation, 671
 Dough, irradiation, 723
 Dragon's blood, 610
 Draper effect, 284, 285
Drosera whittakeri, 502
 Drosone, 502
Drosophila, 703, 765
 Drugs, and light, 268, 657, 658
 Dryco, irradiated, 827
 Drying oil substitute, 584
 "Dual purpose" sources, 142-147
 Duco, nitrocellulose enamel, 586
 Dulcitol, 1,2,5,6-di-*o*-nitrobenzylidene, 472
 Duranthrene yellow, 633
 Europhen lacquer, 592
 Dust, 196, 201, 202, 340
 Dyeing, aniline black, 495
 nitronaphthalene derivatives, 501
 Dyes, absorption, 624
 and carbohydrate photosynthesis, 869, 873
 and cotton tendering, 615, 617, 643
 and gasoline, 657
 and irradiated wool, 622
 and perfused heart rhythm, 761
 and potassium dichromate, 634
 and rubber oxidation, 601, 603, 609, 610
 and Weigert effect, 383
 as photosensitizers, 259, 260, 263, 264, 381,
 556, 712, 745, 832, 862
 associated, 264
 azine, 497
 azo, 624, 630
 Dyes, basic, 485
 diphenylmethane, 640
 direct, 390, 616, 635, 642
 excited, 263, 264
 fading, 103, 205, 206, 259, 384, 631-635, 863,
 864
 fluorescent, 260-264, 463, 600, 645
 for airplane wings, 643
 for balloon fabrics, 608
 for filters, 177, 182, 632
 halogenated, 507
 in paper, 644
 in textile printing, 645
 nitrated, 633
 peroxide formation, 863, 864
 phthalein, 629
 tests for light fastness, 443, 578, 634-642
 Dyes, triphenylmethane, 626-629, 632
 vat, 616, 617, 630, 642, 647
 Dypnone, 490, 494
 Dysentery phage, 712
E
 Earthworm, porphyrin, 767
 Eastman sensitizer, 382
 Eastman UV spectroscopic plates, 160
 Ebonite, 584, 608, 609, 611
 Eclampsia, therapy, 774
 Eczema, 769, 824
 Eder reaction, 443-445
 Edestin, oxidation, 678
 Egg yolk, sterols, 789, 816
 Eggs, 717, 718
 antirachitic properties, 787, 827
 Arhacia, 764
 Chaetopterus, 764
 hatchability, and production, 787, 788
 sea urchin, 764
 starfish, 764
 Eigenfunctions, 26
 Einstein equivalence law, 207, 210, 211, 213, 222
 266, 342, 351, 355, 732, 802, 863, 874
 unit, 207
 Elaidic acid, 565
 Elder blossoms, 657
 Electrical discharges, classification, 30, 32
 Electricity, static, removal from air, 662
 Electrodes, (see also cathodes and mercury arc)
 aluminum, 156, 157, 159
 arrangement for sparks, 42-44
 brass, underwater spark, 153, 155
 carbon, 150
 for discharge tubes, 133, 135, 140, 339, 364
 for many-lined emission, 152
 Electrolysis, intramolecular, 371
 with irradiated cathodes, 339
 Electromagnetic spectrum, 2, 3, 6, 9, 10
 Electrometer, 97
 Electron, accelerated, 8, 9
 affinities, 263, 337, 338, 372, 378, 438
 alloy, 661
 bombardment, 209, 229, 348, 354
 diffraction, 11
 displacements in crystals, 373, 374
 energy levels, 218, 220
 high-velocity, lethal action of, 705
 orbits, 26
 primary, 31
 secondary, 31
 temperature in arc plasma, 48, 94
 transitions, 22-24, 227, 337, 338
 ultimate, 32
 Electron-volt, 8, 220
 Electrophoresis, 387, 388, 704, 751
 Electroscopes, gold leaf, 97
 Elements, discovery, 662
 in sun, 192
 transitional, absorption spectra, 337
 Eleomargaric acid, 564
 Eleostearic acid, 564-566, 574
 Flixir of pepsin, 658
Elodea canadensis, 715
 Embryonation, roundworm ova, 718
 Embryos, 718, 765
 Emetine, 760
 Emission, of radiant energy, quantum theory,
 15-30
 Emulsin, 680
 Emulsions, 391, 657
 gelatin, 266, 379, 380
 of bacteria, 693, 694
 Enamels, accelerated weathering tests, 586, 587
 Enanthaldehyde, 423
 Encephalitis virus, 712
 Encephalomalacia factor, 856
 Endocrine organs, 790
 Energy, and mass equivalence, 191
 intramolecular migration, 427
 levels, 17, 21-23, 26-29, 92, 218-220, 222, 223,
 226, 230
 Engine oil, irradiation of, 653
 Entropy, 217

- Enzymes, 370, 436, 680-688, 727, 853, 891
 and plant photosynthesis, 874, 876, 880
 in blood, 756
 inactivation thresholds, 247
 nucleic acid-splitting, 703
- Eosin, 260, 264, 339, 344, 381, 383, 390, 633
 as sensitizer, 435, 444, 445, 451, 498, 553, 554, 595, 678, 682-684, 688, 703, 725, 812, 817, 862, 863, 865
 in biological stains, 631
 in therapy, 772
 lake, 642
 photolysis, 498
- Ephedrine, 688
- Epichlorhydrin, 497
- Epicholesterol, 792
- Epidermal cells, *Aucubus* leaves, 715
- Epidermis, 693, 735-737, 739, 772, 809
- Epihydrinaldehyde, 553, 560
- Epilepsy, 776
- Equilibrium constants, 217
- Ergometrine, 525
- Ergopinacol, 812
- Ergostatriene, 796
- Ergosterol, absorption spectrum, 795-797
 and corona discharge, 832
 and fermentation, 709
 and tobacco, 660
 as provitamin, 794-803, 813, 814, 816
 color reactions, 796
 dehydro, 810, 812
 22-dihydro, 811-813, 817, 834
 in soaps, 847
 in skin lesions, 742
 irradiated, 782, 800-807, 809-811, 819, 828, 831, 832, 834
 sensitized reactions, 812, 862
 peroxide, 812
 production, 832
 separation from vitamin D, 833
 structure, 795, 796, 809, 811
 unimolecular films, 811
- Ergosteryl acetate, 804, 812
- Ergot, 525, 795, 796, 828
- Ergotetraene, 812
- "Ertron," 832
- Erythema, 673, 733-742, 744, 754, 757, 759, 773, 775
 induratum, 769
 production and reciprocity law, 101
 radiations causing, 103, 105, 197-199, 628
 tests for dosage in therapy, 102, 771, 783
- Erythritol, di-*o*-nitrobenzylidene, 472
- Erythrocytes, 746-750, 758, 818, 860, 863, 865
- Erythrosin, 264, 381, 390, 634
 as sensitizer, 490, 554, 863
 photolysis, 498, 629
- Erythrose, 432
- Escherichia coli*, 693, 694, 698, 704-707, 711, 712, 757, 775
- Esculin, 390, 562, 629, 743
- Eserine salicylate, 522, 726
- Esparto, 644
- Essential oils, 513-515, 727, 728
- Ester gum, 585, 590, 591
- Esters, absorption spectra, 437
 as polymerization inhibitors, 410
 chlorinated vinyl, 410
 formation in plants, 882
 hydrolysis, 436
 in fermentation, 709
- Ethane, 258, 406, 440
 diphenyl and derivatives, 478, 520, 626
 effect on acetone photolysis, 428
 formation, 396-398, 406, 407, 414, 418, 425-427, 429, 431, 448, 458-460, 464
 halogenated, 400, 526, 528, 533-535, 537, 613
 photolysis, 393, 394
- Ethanol, 340, 365, 366, 369, 433, 449, 471, 514
 absorption of light, 401, 402
 addition to crotonic acid, 455
 and chloroform chlorination, 533
 as polymerization inhibitor, 410
 bromination, 538
- Ethanol, formation, 397
 oxidation, 403, 404
 photolysis, 402
 reaction with ketones, 403, 514, 517
- Ether, chloroethyl, 546
 diethyl, 540
 dimethyl, 405, 459
 diphenylallyl, 493
- Ethers, 361, 405, 467, 510
- Ethoxyanilines, 498
- Ethoxybenzylacrylic esters, 491
- Ethyl acetate, 340, 356, 431, 436
 acetoacetate, 431, 630
 alcohol (see Ethanol)
- Ethylamine, 322, 340, 403, 408, 458
- Ethylanthracene, 509
- Ethylbenzene, 488, 546
- Ethyl benzoate, 340
 benzoylacrylate, 491, 492
 bromide, 396
 bromocyclopropanedicarboxylate, 542
 bromopropionate, 266
- Ethylcarbazole, 382
- Ethylcellulose, 463, 591
- Ethylchlorophyllide, 862, 863, 872
- Ethyl cinnamate, 340
 cinnamylidenecyanoacetate, 484
- Ethylcoumaric acid, 488
- Ethyl cyanocyclopropanedicarboxylate, 542
- Ethylcyclopropane, dicarboxylate, 542
- Ethyl diazoacetate, 460
 dibromocyanobutylate, 542
 dihydrocollidine dicarboxylate, 382
 diphenyl-lactate, 493
 diphenylrubrenedicarboxylate, 510
 ether, 540
 fumarate, 454, 455
 green, 634
 iodide, 246, 336, 396, 397
 ketopentadienedicarboxylate, 489
 maleate, 454, 455
 malonate, 540
 mercaptan, 463, 465
- Ethylmethylmaleimide, 872
- Ethyl nitrite, 461
 nitrobenzylidene malonate, 548, 549
 oxalisobutylate, 493
 peroxide, 397
 phenylacetate, 340
- Ethylphenylanthracene, 508
- Ethylphenylindone, 493
- Ethyl radical, 396, 408
 red, 381
- Ethylthiolactic acid platinum, 464
- Ethyl toluidenebutylate, 456
- Ethylene, 393, 406-408, 440, 833
 and methylene radicals, 430
 formation, 396, 398, 399, 414, 422, 429, 430, 458, 460, 514
 halogenation, 534, 537
 hydrogenation, 258
- Ethylene, benzoyl derivatives, 489, 490, 493
 biphenylene, 408, 490
 dibromo, 537
 dichloride, 534, 535, 537
 diiodide, 399, 400, 536, 537
 dimethyl, 429
 glycol, 399, 404, 407, 408, 410, 562, 660
 oxide, 493, 612
 perchloro, 657
 phenyl, 488
 tetrachloro, 534, 535, 657, 659
 trichloro, 529, 535, 657
 trimethyl, 594
- Etioglucobilin, 680
- Etioneoxanthomethenes, 680
- Etioporphyrin, 680, 872
- Eucalyptus oil, 513
- Euchoris multicornis*, 767
- Eugenol, 513, 514
- Euglena*, lethal action on, 713, 888
- "Eveready" therapy units (see Carbon arc)
- "Everfast" suitings, 616
- Excited molecules, 214-216, 242, 251
 states, 220, 226, 232, 243

- Exciton, 375, 379
 Exclusion principle, 25
 Excreta, antirachitic action of, 780
 Exploded wire, ultraviolet source, 35, 36
 Explosions, 209
 Explosives, smokeless, 462
 Extinction coefficients, 249, 250, 271
 Eye media, 762-764
 Eyes, protection from radiations, 164
- F** acid, and photopyridine, 519
 F color centers, 373, 374, 375
 Fabrics, 188, 189, 613-617, 621, 635, 645
 Fade-O-meter, 508, 578, 608, 616, 617, 622, 623, 633-635, 641-644
 Falk electrophoresis cells, 704
 Faraday dark space, 30, 31
 Farina, irradiated, 830
 Farmer's skin, 769
 Fast Orange, 634, 639
 Fast Scarlet, 5, 639
 Fat, absorption spectrum, 670
 and erythema, 741
 and milk irradiation, 762, 844
 beef, 559, 560
 fluorescence, 556, 600
 formation in plants, 882
 irradiation, 789, 827, 831
 metabolism, 826
 oxidation, 559
 sterilization, 721
 Fatty acids, 508, 553, 554, 559, 652, 669
 Fehling's solution, 614
 von Fellenberg test, 561
 Fenchone, 514
 Fermentation, 432, 660, 709, 710, 826
 Ferns, prothallia of, 714
 Ferric acetyl acetone, 465, 595
 chloride, 205, 410, 411, 469, 503, 531, 532, 539, 544, 553
 and chlorophyll, 872
 and gelatin, 384
 and rubber, 595
 as sensitizer, 441, 442, 867
 catalyst, 883
 crystal, light absorption, 360
 photolysis, 360, 361
 reduction by organic acids, 441, 443, 448, 450
 gluconate, 451
 hydroxide, and cotton, 614, 615
 catalyst for photosynthesis, 868, 870
 sol, 389-391
 ion, 344, 360, 448, 451, 631
 nitrate, 522
 oxalate, 255, 445
 oxide, 167-169, 171, 577, 870
 resinate, 619
 salts, 361, 362, 384, 444, 449-459
 sulfate, 359, 362
 Ferrieyanide ion, 341, 362, 363
 Ferrites, 173
 Ferrocyanide, 341, 354, 362, 363, 630
 Ferrocysteine-carbon monoxide compound, 687
 Ferrous acetyl acetone, peroxide, 465
 carbonate, 831
 chloride, 361, 367, 553, 872
 hydroxide, 360, 362, 450
 iodide, oxidation, 254
 ion, 263, 344, 360, 439, 455, 686, 881
 oxide, 167, 168
 resinates, 619
 salts, 444, 449, 588, 589, 669, 702, 868
 sulfate, 359, 360, 364, 443, 455, 631
 action of X-rays on, 209
 and chlorophyll, 871
 oxidation by benzoquinone, 480
 reaction with iodine, 344, 345
 sulfide sol, 390
 thiocyanate, 358
- Fertilizers, 662
 Fertilizin, 764
 Fibrinogen, 676, 678, 825, 862
 Films, photographic, transparency, 585
- Filter, 177-189
 ammonium thiocyanate, 347
 and irradiation of marine organisms, 717, 718
 benzene, 799, 829
 caffeine, 370
 carbon disulfide, 833
 chlorine, 314, 800
 cobaltous sulfate, 347
 copper sulfate, 347
 Corning G 586 AW, 889
 for accelerated paint tests, 580
 for actinometry, 102, 103
 for irradiating ergosterol, 833
 infrared, 126, 178, 186
 in irradiating foods, 828, 829
 in measuring energy distribution, 96-101
 in studies of bacterial action, 692
 lead acetate, 726
 methylene blue, 744
 nickel oxide, 663
 paper, 619
 photographic, 178, 632
 potassium nitrate, 800
 quinine sulfate, 347
 Schott glass, 864
 silver-leaf, 150, 178, 762
 to remove rays shorter than 3200 Å., 150
 Wood's glass, 781
 xylene, 829
- Filtray A, 166
 Fish, antirachitic potency, 827
 oils, absorption bands, 853
 Fish-livers, origin of vitamin D, 790
 Flagella formation, 767
 Flaking of paints, 577
 Flames, 35, 663
 Flaming arc (see Carbon arc, flaming)
 Flannel, 188
 Flavanthrene, and cellulose, 635
 Flavin, 686, 850-853, 857-859
 Flax, 613, 645
 Flex-o-glass, 170
 Flexometer, 587
 Floridin, 794
 Floridoside, 436
 Flour, bleaching, 45, 722
 Flowers, 178, 715
 Fluoray, 664, 852
 Fluorene, 382, 490, 504
 amino, 511
 phenyl, 512
 Fluorene, 476, 477, 511
 Fluorescein, 260, 262, 339, 390, 864
 as sensitizer, 725, 865
 destruction, 629
 sodium, 864
 surface tension, 503
 Fluorescence, 105, 150, 207, 213-215
 and Eder reaction, 444, 445
 and nature of spectra, 230, 231, 242, 243
 and sensitization, 260-263, 862
 and tetraphenylrubrene oxidation, 510
 analysis, 178, 575, 663-665, 852
 in tanneries, 651
 of dyes, 645
 of fats and oils, 556, 557, 559
 of ink, 644
 of lacquers, 591
 of paper, 620
 of resins, 158
 of rubber accelerators, 600, 601
 of textiles, 624
 assay, flavins, 852
 benzene, 466
 catalase, 685
 Chlorella, 877
 chlorophyll, 864, 877, 878
 efficiency, 261, 262
 glass, 176
 hydrogen peroxide, 304
 in radiation measurement, 100
 of skin, 734, 735
 phosphoride-b, 879
 quenching, 231, 257, 260-264, 335
 textiles, 624

- Fluorescence, theory, 261, 665
 ultraviolet, in biology, 733
 yeast respiratory enzymes, 687
 Fluorescent lamps, 142, 152
 Fluorides, 171, 172, 657
 Fluorine, 238, 274, 317
 oxide, 349
 Fluorite, 7, 151, 208, 349, 698
 Fluoroheptachlorocyclohexane, 344
 Fluorometers, 105
 Fog nuclei, 387
 Follicular hormones, 689
Fomes pini, 889
 Foods, irradiation, 721-724, 788-791, 827-831
 Foot-and-mouth disease, virus, 712
 Forbidden lines, 24, 92
 Formaldehydes, 173, 258, 308, 310, 315, 316, 368, 435, 439, 573, 612, 705, 883
 absorption spectrum, 416
 and ammonia, 522
 and lethal action of radiations, 695
 and nitrites, 882
 and tryptophane oxidation, 671
 condensation with urea, 584
 conversion to alcohol, 418
 dissociation, 240
 formation, 72, 308, 396, 397, 399, 400, 402, 403, 428, 433, 434, 439, 441, 451, 462, 465, 525, 873
 from egg albumin, 676
 in atmosphere, 194, 869
 in plant photosynthesis, 866-870, 877, 880
 oxidation, 418, 422, 434
 photolysis, 240, 416, 417, 420, 422, 425
 polymerization, 416
 production from water gas, 259
 reaction with chlorine, 418
 reduction of tungstic acid, 387
 Formamide, 322, 458
 Formhydroxamic acid, 882
 Formic acid, 308, 369, 418, 469, 584, 695, 878, 883
 absorption spectrum, 437
 and chlorophyll bleaching, 872
 chlorination, 539, 540
 -formate buffer, 364
 formation, 399, 404, 407, 422, 440, 460, 467, 468, 480
 in plant photosynthesis, 867, 868, 880
 oxidation, 440
 photolysis, 246, 422, 437, 439, 440
 Formose, 867
 Formyl chloride, 418
 Fractures, healing rate, 819
 Franck-Condon principle, 236, 242
 Franck-Haber theory, 355
 Fraunhofer lines, 4, 6, 18
 Free energy, 217
 radicals, 231, 397, 421, 424-426
 Frequency, 5
 Friedlander's bacillus, 720
 Frog eyes, oxygen uptake, 764
 larvae, 765, 766
 muscle, 678
 Frost injury of plants, 887
 Fructose, 432-434, 521, 710, 867, 883
 nitrobenzylidene acetal, 472
 Fruit, composition after irradiation, 891
 juices, sterilization, 722, 725
 Fuchsin, 179, 182, 264, 382, 498, 629
 Fucoxanthin, 882
 Fulgides, 493
 Fumaric acid, 412, 451-455, 541, 764
 Fumaronitrile, 457
 Fundamental frequency, 233-235
 series, 23, 24
 Fungi, 711, 860, 886, 889, 890
 Fungisterol, 796
 Furandicarboxylic acid, 515
 Furazan, diphenyl, 498
 Furfural, stability, 466
 resins, 584
 Furoperacid, 517
 Furunculosis, 769
Fusarium, 711
- G** acid, 382
 Gadolinium compounds, 142
 Gaede pump, 148
 Gaertner bacillus, 758
 Galactose, 432, 433, 521, 752, 883
 nitrobenzylidene acetals, 472
 Gallacetophenone, 498
 Gall bladder, 826
 Gallium, in cadmium lamp, 150
 Gallocyanine, 632
 Galloflavin, 479
 Gametes, of *Chlamydomonas*, 767
 Gamma-rays, 2, 7, 9
 Gas, electrolytic, 310
 inert, 77, 131, 132, 138, 296, 297
 ionization, 269
 irradiation apparatus, 70, 71
 natural, chlorination, 526-528
 Gas gangrene bacillus, 710
 Gasolines, 503, 651, 657, 665
 Gastric juice, 677
 secretion, 759, 760
 Gastrulation, 718
 Geelgikup, 861
 Geiger-Müller counter, 100, 768
 Geissler tube, 30
 Gelatin, 363, 481, 620, 645, 662, 676-679, 688, 727
 absorption of ultraviolet rays, 7
 and cobra venom, 691
 and diastase, 682
 and lead arsenite papers, 359
 and silver nitrate, 383
 and silver sols, 388
 and Weigert effect, 383
 chromate reaction, 365
 emulsion, 266, 380
 ferric chloride reaction, 384
 films, 562, 585, 632
 filters, 177, 182, 183-186
 gel, 389
 in paper, 619
 Gels, Liesegang rings in, 391
 Gentian violet, 634
 Gentianose, 435
 Gentiopicroin, 436
 Gentisic acid, 479
 Geraniol, 514
 Geranium, plants, 886
 Germane, 333
 Germinating layer, of skin, 736
 Germination, 716, 849, 885, 886
 Getter, 138
 Ghee, 856
 Glands, of internal secretion, 688, 689, 759, 760
 Glass, absorption of ultraviolet rays, 7, 164, 168-176
 American Optical Co. Nos. 57 and 58, 165
 and drug deterioration, 657, 658
 and dye fading, 637, 639
 and gasoline color stability, 653
 barium, 165, 201
 beryllium, 170-172
 black, 167, 187
 bonding with rubber, 611
 Chance's, 100, 187
 cobalt, 165, 168
 colored, and paper, 620
 Corex, 100, 101, 103, 143, 146, 169, 170, 173-175, 179, 181, 185, 325, 637, 653, 704, 781, 843, 844
 Corning, 165, 174, 186, 187, 580, 782
 Crookes, 164-166
 didymium, 177, 178
 filters, 164, 177-181, 188, 664, 711, 889
 for seals into quartz, 75
 for sunlamp, 143, 146
 fluorescent, 142, 176, 663
 Gétan, 172
 heat-transmitting, 165
 Helio, 174, 175, 181
 infrared absorbing, 164
 laminated, 167, 411, 591
 lead, 148, 165
 lime, 165

- Glass, lithium, 168, 172
 Locke, 174, 175
 magnesium, 170
 manganese, 176
 microscope, 181
 neodymium oxide, 178
 nickel, 168
 Nonex, 75
 Noviol, 165, 180, 187, 188, 886
 Noviweld, 165
 optical crown, 165, 166, 180
 phosphate, 132, 133, 168, 172, 176
 plate, 176
 powdered, in rubber, 610
 protective, 164-167
 Pyrex, 72, 75, 103, 146
 quartz, 173, 175
 Schott, 175, 864
 sextant, 165
 soda-lime, 148, 165, 166, 168, 175, 176
 solarization, 174-176
 Uviol, 156
 Vita, 103, 104, 169, 172-175, 178, 181, 637, 661, 711, 712, 776, 782, 825, 887, 888
 window, 103, 169, 170, 173-175
 zinc, 165
 Glucobilin, 680
 Globin, ammonia formation, 676
 Globulin (see Serum globulin)
Glomerella, 890
 Glow discharge, 30-32, 47, 93, 131, 136-141, 146
 hydrazine formation in, 319
 in gasoline treatment, 655
 in vitamin D production, 804, 832
 nitrogen dioxide synthesis by, 327
 Glow lamp, 132, 138-141
 Glucolysis, 710, 857, 858
 Glucosamine, 433
 Glucose, 369, 387, 432-436, 686, 688, 710, 883
 and pyridine, 521
 fermentation, 709
 phenylazone dicarboxylic acid, 183
 photosynthesis, 867
 tolerance, 752
 Glucosides, 432, 436
 Glucuronic acid, 435
 Glucuronosidase, 684
 Glue, 612, 619
 Glutacondialdehyde, ammonia derivative, 519
 Glutamine, 883
 Glutaric acid, 441
 Gltathione, 432, 680, 743, 751, 760, 761, 764, 825
 Glyceric acid, 404
 aldehyde, 402, 404
 Glycerides, 554
 Glycerol, 185, 260, 339, 353, 361, 385, 523, 612, 645, 660, 737, 791, 883
 from lecithin, 669
 oxidation, 404, 559
 photolysis, 402, 403
 preparation, 407
 Glycerol butyl phthalate, 592
 nitrobenzylidene benzoyl, 472
 phthalic anhydride resins, 585
 salicylate, 743
 Glycerophosphatase, 818
 Glycerophosphoric acid, dehydrogenase, 687
 Glycerose, 339
 Glycerosone, 431
 Glyceryl acrylate, 456
 galactoside, 436
 Glycine, 260, 671, 672, 677, 681
 Glycogen, 436, 706, 742, 752, 753
 Glycol, 402, 405, 407, 472, 656
 Glycolaldehyde, 404
 Glycol, dipropyl, 403
 methyl phthalate, 591
 nitrobenzylidene, 472
 peroxide, 402
 salicylate, 743
 vinyl ether, 411
 Glycollic acid, 451, 671, 867
 Glycolysis, and sensitizers, 863
 Glycosuria, 752
 Glycylglycine, 436, 672
 Glycyltyrosine, 436
 Glyoxal, 404, 415, 431, 450, 451
 Glyoxalic acid, 869
 Glyoximes, 461
 Glyoxylic acid, 451
 Goats, 861
 Goitre, 689, 777
 Gold, 142, 165, 178, 366, 377
 chloride, 371, 391, 522, 605
 salts, 359, 388
 sol, 388-391, 669, 677
 Goldfish, 402
 Grains, photographic, 379, 380
 Granatum, tincture, 658
 Graphite, 253, 341, 612
 Graphitic acid, 64
 Grass, 790
 Grass-bleaching, 615
 Gratings, diffraction, 4, 6, 7
 Grignard compounds, 464
 Grotrian diagrams, 27-29
 Grothuss-Draper law, 205, 206
 Ground state, 220, 232, 237
 Growth, 58, 150, 759, 886-888
 Growth-substances in irradiated cells, 708, 709
 Guaiacol, 513, 726
 Guaiaconic acid, 479
 Guaiaretic acid, 479
 Guanidine, 458, 672
 derivatives, 592, 605, 610, 612
 Guanine, 672, 699, 701, 703
 Guard cells, of leaves, 715
 Guinea Green, 634
 Gum, 585, 589
 arabic, 363, 387
 formation in gasoline, 653-656
 in enamels, 590
 mastic sol, 387, 390
 tragacanth, 612
 Gutta-percha, 593-595, 604

H acid, 647
 Haber-Willstätter mechanism, 403
 Hair, yellowing, 744
 Halibut liver oil, 816
 Halo-acetic acids, and alcohol, 452
 Halogenated acids, 451, 452
 Hammerscale, 583
 Hanovia lamp, 78, 79, 81, 129, 184, 837 (see also Mercury arc)
 Harmonic oscillator, 232, 233, 235
 Hartack xenon lamp, 393
 Hatchability of eggs, 787, 788
 Hausmann numbers, 365
 Hay, 790, 817
 Hay fever, 776, 824
 Heart, 733, 750, 760, 761, 862
 Heat of reaction, 245
 Heats of dissociation, 217, 235-237, 241, 243, 246, 247
 Heavy water, and plants, 882
 Hectograph pads, 645
 Heimsonne, Alpina, 132-134
 Heisenberg uncertainty principle, 236, 243
 Helianthine, 631
 Helianthone, derivatives, 506, 507
Helianthus annuus, 882
 Helicin, 436
 Helioglass, 173-175, 181
 Heliotherapy, 733, 734, 770
 Helium, 27, 33, 138, 139, 144, 150, 151, 192, 279, 280
 effects on various reactions, 273, 296, 327, 329
 Hematin, 622, 748, 750
 Hematoporphyrin, 263, 264, 671, 673, 678, 749, 751, 852, 860-863, 865
 Hemin, 553, 685, 687, 749
 Hemochromogen, 690, 750
 Hemoglobin, 679, 680, 687, 688, 746, 748, 749, 791
 Hemolysins, anti-sheep, 758
 Hemolysis, 669, 750, 860, 862, 864, 865
 Hemp, 613, 620, 645
 Hemsalech coil, 41
 Henna, use as protective pigment, 861

- Hepatoflavin**, 851
Heptachlorocyclohexane carboxyl chloride, 547
Heptane, 394
 iso, 530, 531
Heptylene, 394
Heraeus lamp, 78, 147
Heroin, 726
Herpes, 712, 769
Herschel effect, 256, 380
Herzberg bands, 294, 295
Heteropolytungstic acids, 369
Hexamminecobaltic chloride, 368
Hexachlorocyclohexane carboxyl chloride, 547
Hexachlorodisilane, 64
Hexadecylpyridinium bromide, 644
Hexadiene tetraphenyl, 411
Hexahexosan, 435
Hexahydrobenzene, 211, 466
Hexahydroethylbenzene, 473
Hexane, 182, 393, 394, 429
 chlorination, 526, 530
 nitration, 470
Hexatungstic acid, 369
Hexene, 536
 dimethyl, 461
Hexose, photosynthesis, 868, 870, 878
 phosphates, 432
Hexosephosphatase, 818
Hexuronic acid, 849
Hexyl chloride, 531
Hides, 650, 651
High-frequency field, 36
Hilger monochromator, 190
 spectrograph, 160
 Vitameter, 853
Hippuric acid, 672
Histamine, 672, 673, 677, 733, 740, 741, 749, 759
Histazarin dimethyl ether monoxime, 522
Histidine, 672, 673, 676, 677, 703, 740, 741, 748, 882
Höhensonne lamp, 695
Hofmann violet, 634
Holvglass, 171, 173
Homatropine, 658
Homotropococaine, 436
Hordeum seedlings, 888
Hormones, 688-690
Horn, 678
Hospitals, ultraviolet sterilization in, 728-731
Howland color photometer, 583
Humidity, and dye fading, 636, 641, 642
 and meat tenderizing, 724
 and rayon deterioration, 621
 in accelerated paint tests, 577-579
Humus, 350
Hydantoins, 518, 702
Hydrastinine, 523
Hydrastis, tincture, 658
Hydrates, 437
Hydrazine, 258, 318-323, 363, 371
Hydrazobenzene, formation, 500
Hydrazones, phototropy, 493
Hydriodic acid (see **Hydrogen iodide**)
Hydroa, 861
Hydrobromic acid (see **Hydrogen bromide**)
Hydrocarbons, aliphatic, 531
 aromatic, 466-469, 655
 chlorinated, stabilizing, 657
 cyclic, absorption spectra, 651
 formation, 64, 425, 437, 438, 448, 459, 460, 464
 fuels, 652
 in arc, 60
 liquid, 394, 531
 saturated, 393-395, 449, 529
 unsaturated, 393, 438, 449, 531, 533-538, 655
Hydrocellulose, 618
Hydrochloric acid (see **Hydrogen chloride** and **Hydrogen-chlorine combination**)
Hydrocinnamaldehyde, 473
Hydrocinnamic acid, 340, 482, 548
Hydrocyanic acid (see **Hydrogen cyanide**)
Hydrogen, 144, 192, 211, 214, 279, 291, 345, 360, 362, 370, 393, 414, 440, 466, 471, 481, 614, 615-650, 652
 active, 37
 and dyes, 633
 and ethylene reaction, 406-408
 and gutta-percha, irradiation, 594, 595
 and hemoglobin, 680
 and nitrogen, 318
 and paper, 619
 and rubber, 601
 atomic, 244, 283, 290, 301-305, 309, 310, 313, 316-323, 438, 439, 472, 540, 560, 811, 877-879
 atoms, recombination, 163, 213, 319
 by operating carbon arc under water, 64
 -chlorine combination, 105, 205, 209-211, 213, 218, 244, 246, 253, 255, 281-291, 302, 306, 315
 discharge, 152, 156-162, 208, 270, 698
 dissociation, 163, 229, 231, 237, 272
 effects on various photoreactions, 296, 297, 315, 316, 318, 321, 324, 327, 328, 332, 333, 357, 358, 375, 385, 397, 400, 427, 460, 462, 534, 537, 869
 formation, 339, 349, 396, 398, 399, 402, 406, 416, 417, 420-422, 427, 431, 432, 438-440, 448, 449, 451, 458, 461, 463, 465, 514, 864
 balises, 272-280
 in gasoline testing, 653, 654
 in metal-vapor lamps, 150
 ionization potential, 27
 ortho, 226
 oxidation, 250, 257, 258, 289, 299-305, 310
 para, 226
 reaction with amino radical, 319, 321
 reaction with atomic chlorine, 316
 reaction with carbon dioxide, 308
 reaction with carbon monoxide, 310
 reaction with fluorine, 274
 reaction with iodine chloride, 280
 reaction with nitrous oxide, 325
 reaction with sulfur, 329
 resonance potential, 27
 reduction of sodium molybdate, 369
 spectra, 20-22, 33, 156, 162, 163, 272
 -transferring coenzyme, 688
 zero-point energy, 290
Hydrogen compounds,
 azide, 323, 324, 384
 bromide, 413, 492, 498, 506, 508, 541, 542, 545, 546, 550
 absorption spectrum, 275
 and isostilbene, 548
 photolysis, 211, 212, 272, 274, 275
 photosynthesis, 214, 254, 275-280
 chloride, 187, 315, 346, 366, 369, 508, 527, 528, 530, 531, 537, 539, 544, 546, 548
 absorption spectrum, 239, 281, 343
 and potassium anthraquinone sulfonate, 506
 and pyridine, 518
 and quinine, 523
 dielectric constant, 239
 effect on Cl_2 -sensitized chloroform oxidation, 314
 formation, 394, 395, 400, 418, 440, 529, 532, 550
 in reactions of amines, 497
 photolysis, 239, 272, 274, 275, 281
 synthesis (see **Hydrogen-chlorine combination**)
 cyanide, 62, 363, 451, 456, 458, 498, 875-877, 891
 iodide, 249, 396, 520, 533
 absorption spectrum, 156, 230, 272
 and methyl iodide, 397
 formation, 274, 400, 498, 595
 photolysis, 211, 212, 215, 255, 272-274, 342
 photooxidation, 305
 peroxide, 346, 383, 407, 411, 433-435, 449, 556, 629, 633, 649, 657, 673, 789, 864, 883
 absorption spectrum, 303, 304, 339, 341
 and adrenaline, 688, 689
 and carbohydrate photosynthesis, 868, 876-880
 and *Chlorilla*, 875
 and cholesterol, 834
 and dyes, 616, 634
 and hemolysis, 865
 and insulin, 679
 and lethal action of radiations, 695

- Hydrogen peroxide (*Continued*)
 and milk irradiation, 722, 840
 and pyridine, 519
 and silver sols, 388
 and soy bean oil, 573
 bleaching by, 618
 dissociation, 304, 339
 emission spectrum, 304
 formation, 299, 300, 302, 339, 604
 in actinometry, 341
 in carbon monoxide oxidation, 309, 310
 in forming metal sols, 387
 in sensitized oxidations, 258, 863
 in water photolysis, 299
 inhibitor of Eder reaction, 445
 oxidations by, 304, 418
 photolysis, 209, 253, 254, 267, 304, 305, 339-341, 410
 reaction with hydroxyl radical, 340
 reaction with oxygen, 340
 sensitizer for ethanol oxidation, 403
- Hydrogen sulfide, 354, 359, 367, 390, 407
 absorption spectrum, 329, 336, 355
 and plant photosynthesis, 875
 and vitamin C, 848
 formation, 599, 623, 654
 in paint tests, 580
 photolysis, 329, 330, 355
- Hydroquinol, 509
- Hydroquinone, 356, 390, 421, 439, 604, 631, 688
 and polymerizations, 410, 595, 596
 formation, 482
 in vitamin D preparations, 833
- Hydroxamic acid, 882
- Hydroxy acids, 440, 448-450
- Hydroxyanthraquinone, 507
- Hydroxyazobenzene, 470, 496, 499, 562
- Hydroxyazobenzene, 470, 496, 499, 562
- Hydroxybenzoic acid, 480, 500, 546
- Hydroxybiphenyl, sodium sulfonates, 743
- Hydroxychlorophyll, 878, 879
- Hydroxycholesterol, 792
- Hydroxycinnamic acid, 484
- Hydroxylmethylamine, 497
- Hydroxydroserone, 502
- Hydroxyisotogenic acid, 482
 (Hydroxyethyl)isoxaloxazine, 852
- Hydroxyl ion, absorption spectrum, 338
 radical, 299, 301, 302, 305, 397, 438, 439
 reactions of, 304, 305, 309, 340, 438
- Hydroxylamine, 323, 371, 458, 877, 883
- Hydroxymethylene camphor, 515
- 4-Hydroxy-2-methyl-N-phenylmorpholine, 612
- Hydroxynaphthaquinone, 502
- Hydroxynaphthylchromic acid, 503
- Hydroxynicotinic acid, 702
- Hydroxyoleic acid, 553, 559
- Hydroxyphenazine, 522
- Hydroxyphenylenediamine, 498
- Hydroxyphenylpropanolamine, 689
- Hydroxyproline, 672, 676
- Hydroxyquinoline sulfonic acids, 183
- Hydroxysiloxene, 333
- Hydroxystearic acid, 560
- Hydroxystyrylmethyl ketone, 489
- Hyperemia, 734, 741, 746
- Hypericum, photosensitizer, 861
- Hypertension, therapy, 774
- Hyperventilation, 753
- Hypnone, 513
- Hypobromous acid, 455
- Hypochlorous acid, 307, 346, 618
- Hypodite, 343
- Hyponitrous acid, 350
- Hypophysis, 690, 790
- Illuminating sources, nature of, 15
- Imidazoleacetaldehyde, 673
- Imidazoleethyl alcohol, 673
- Iminodibutyric acid, 455
- Immune sera, 706, 757-759
- Incandescent lamps, 152, 156
- Indanthrene Yellow, 616, 633
- Indazole, substituted, 743
- Indene, 431, 517
- Indicators, fluorescent, 665
- Indigo, 616, 622, 633, 638
- Indigocarmine, 631, 637, 640, 642
- Indigocarmine blue, 634
- Indigosol, 632, 645, 647
- Indium oxide, 360
- Indole derivatives, 517, 671, 743, 887
- Indones, 453, 492, 493, 517
- Indophenol oxidase, 686
- Inductance, 91
- Induction coils, 40, 42, 76, 125, 136, 148, 149, 152
- Induction period, 205, 253, 255, 434, 441, 532, 540
 acrolein polymerization, 424
 alcohol-benzophenone reaction, 480
 carotene oxidation, 856
 chloroprene polymerization, 596
 cinnamic acid bromination, 486
 Eder reaction, 445
 fat oxidation, 840
 gum formation in gasoline, 655
 hydrogen-chlorine combination, 281, 285-286
 in plant photosynthesis, 871, 872, 877, 881
 in stereoisomerizations, 485, 518
 lactic acid photolysis, 449
 oxidations, 449, 627
 ozone photolysis, 297
 phosgene formation, 311, 313
 succinic acid-methylene blue reaction, 447
 tartaric acid bromination, 541
 vitamin A photolysis, 855
- Indulant ulcers, 769
- Induline, 634
- Infections, 775, 825
- Influenza bacillus, 669, 750
 virus, 712, 731
- Infrared radiations, 2, 6, 92, 115, 194, 381, 660
 absorption, 165, 220, 222, 224, 225, 235
 effects of, 208, 209, 255, 256, 734
 filters, 178, 183
 in vitamin D production, 828, 832, 840
- Inhibition of reactions by light, 255
- Inhibitors, 214, 252, 253, 356, 357, 365
 benzaldehyde oxidation, 474
 chloroform chlorination, 533
 hemolysis, 862
 hydrogen-chlorine combination, 283, 285, 287, 302
 hydrogen peroxide photolysis, 340, 341
 of polymerizations, 410
- Inks, 641, 644, 645, 648
- Inosine, 710
- Insolameter, 636
- Inulin, 679, 727, 751, 752
- Inulin, 436
- Intensimeter, 100
- Intensity, of light and reactions, 205, 206, 251, 252
- Intercombination lines, 29
- Interferometer, 4, 5
- Interhalogen compounds, 280
- Intermediates, in reaction kinetics, 277
- Interrupters, 76, 77, 92, 154
- Intestinal mucosa, villikinin, 689
- Intestine, effects on, 760
- Intramolecular electrolysis, 371
- Intramolecular migration of energy, 247, 248
- Invar, 74
- Inverse square law, 692, 771
- Invertase, 247
- Iodates, 343, 348, 617
- Iodide ion, 262-263, 337, 338, 342-344, 363, 439, 681, 684
- Iodination of paraffins, 533
- Iodine, 187, 359, 371, 534, 550, 648, 680, 745
 absorption spectrum, 230, 235, 237, 272, 273
 action of x-rays on, 209
 and butene, 536
 and catalase, 685
 and formaldehyde photolysis, 422
 atoms, 254, 536, 537
 absorption, 231
 and oxalate ion, 446
 excitation energy, 237-239, 272, 344, 373
 recombination, 273, 446, 536
 decolorized solution, 658

- Iodine, dissociation, 273
 distribution, 689, 713, 759, 760, 777
 effects on photolyses, 399, 535, 536
 excited molecules, 274, 536, 537
 fluorescence, 231, 272, 273
 formation, 342-343, 396-400, 439, 440, 520, 554, 629
 heat of dissociation, 237
 in discharge tubes, 141
 photochemical oxidations, 249, 446, 849
 photoionization threshold, 269
 photosensitizer, 484, 485, 491, 518, 522, 536, 554, 574
 reaction with alcohols, 345, 538
 reaction with ferrocyanide, 363
 reaction with ferrous sulfate, 344, 345
 reaction with formates, 252, 344, 345, 440
 reaction with nitrites, 249, 344, 345, 351
 reaction with oxalates, 254, 344, 345, 445-447
 sorption on cotton, 615
 Iodine chloride, 280
 green, 634
 pentoxide, 399
 Iodoacetic acid, 876
 Iodoaniline, isodiazotate solution, 646
 Iodobenzene, 246, 474
 Iodoform, absorption spectrum, 395
 action of x-rays on, 209
 and cholesterol, 812
 oxidation, 253
 photolysis, 397, 400
 Iodopropionic acid, 439
 Iodopsin, 857
 Iodopyridinecarboxylic acid, 520
 Iodostarin, 554
 Iodovinylacetylene, 415
 Ionization, atoms, 26, 27, 31, 48, 230
 potentials, 27, 372, 379
 Ion-molecules, 237
 Ionone, 855
 Iridium compounds, 360, 415
 Iris, 164, 763
 Iron, 171, 173, 359, 415
 arc, 46, 47, 49, 50, 693
 chlorination catalyst, 534
 compounds, and paper, 142, 619, 710
 corrosion, 661
 halides, in polymerizations, 411
 ions, 337, 678
 irradiated, 748
 plates, and aniline, 495
 salts, 360-362, 370, 403, 432, 448, 498, 727, 863
 spark apparatus, 38, 39, 152, 154
 spectrum, 23, 26
 Iron acetate, 441
 carbide, in carbon arc, 58
 carbonyls, 514, 545, 749
 chlorides, 514, 545, 749
 citrate, 441
 mercaptide, 465
 mercaptotricarbonyl, 465
 naphthenate, 592
 oxalate, 441
 oxides, 167, 171, 173, 508, 563, 583, 612
 porphyrin compound, 685
 succinate, 441
 tannin compound, 651
 tartrate, 441
 Irradiated air, and rickets, 788, 789
 cholesterol, 791, 826, 847 (see also Vitamin D)
 dried milk, 839
 ergosterol, 819, 820, 825, 831, 833, 834 (see also Vitamin D)
 milk, 789, 841, 844
 skin, and rickets, 779
 yeast, 789, 837
 Irradiation, and resistance to infections, 773, 825
 and rickets, 778, 779
 apparatus, with filters, 184, 185
 lamps, for photochemistry, 139
 of foodstuffs, 788-790, 827
 of gas, 70
 processes, spectrographic control, 833
 with restricted wave-lengths, 828
 Isatin, 633
 Isoalloxazine derivatives, 852
 Isoamyl chloride, chlorination, 527
 Isoamylamine, 264, 864
 Isobutane, 421, 422, 526, 531, 532
 Isobutyl magnesium bromide, 464
 Isobutylidenecholesterol, 817
 Isobutyric acid, 540
 Isochlorophylline, sensitizer, 451
 Isochromatic plates, 381
 Isocinnamic acid, 484
 Isocrotonic acid amide, 455
 Isocyanine dyes, 381
 Isodiazotates, 646
 Isoelectric point, 675, 676
 Isoergosterol, 796, 797
 Isoeugenol, 469, 514
 Isoheptane, 530, 531
 Isomaphthazarin, 502
 Isopentane, 526, 527
 Isophotosantonin acid, 516
 Isophthalic acid, dihydro, 481
 Isoprene, 413, 514, 593-595
 Isopropanol, 357, 402-404, 476, 477, 480, 538
 Isopropenylmethyl ketone, 429
 Isopropyl alcohol (see Isopropanol)
 Isopropyl bromide, 399
 cyclopentanone, 516
 iodide, 396, 398
 Isopulegol, 469
 Isopulegone, 469
 Isopurpuric acid, 498
 Isopyrocalfiferol, 810-812
 Isoquinoline red, 264
 Isostilbene, 511, 548
 Isotopes, 217, 227
 Isouracil, 703
 Isovaleraldehyde, 422
 Issoglio test, 560
 Itaconic acid, 454

J
 Jams, sterilization, 722
 Japan wax, light absorption, 586
 Jara-jara, 558
 Jars, Leyden, 149, 154
 Jellies, sterilization, 722
 Juglone, 680
 Jute, 613, 618

K
 Kala-azar, 777
 Kalicrein, 691
 Kaolin suspensions, 391
 Kaposi's disease, 861
 Kauri gum, 585
 varnish film, 587
 Keratin, 651, 678, 679
 Keratoses, 766
 Kerosene, 533, 653
 Ketene, 428, 430, 431, 440
 Keto acids, 393, 451, 562
 7-Ketocholesteryl acetate, provitamins from, 817
 4-Keto-N-ethylphenazine, 522
 Ketogluconic acid, 451
 Ketohydroxystearic acid, 574
 Ketoketenes, 430
 Ketone, 393, 464, 476-478, 500, 547
 absorption spectra, 415, 416, 425
 diethyl, 341, 421, 428
 diisoxazole, 517
 dimethyl, 341
 diphenyl, 595
 dipropyl, 429
 formation, 450, 657
 -furfural resins, 585
 isopropenylmethyl, 429
 methylbutyl, 421, 429
 methylheptyl, 341, 421, 429
 methylisobutyl, and anisaldehyde, 494
 methylpropyl, 429
 nitrophenylethyl, 478
 phenylmethyl, 477
 propenylmethyl, 429
 photolysis, 421, 425-431
 reactions with alcohols, 403, 404, 517
 styryl, 489, 493, 494

- 2-Keto-*N*-methylphenazine, 522
 Ketopentose, from formaldehyde, 867
 Ketovaleric acid, 451
 Ketoses, 432, 869
 Khaki, 615
 Kidneys, 818, 820, 822
 Kieselguhr, 867, 870
 Kiton Red, 628
 Knop's solution, 887
 Koji extract, fermentation, 709
 "Kojic acid," 630
 Kraft, sulfate, 618
 Kromayer lamp, 57, 126, 127, 735, 744, 769, 770, 797
 Kreis test, 559, 560
 Kryptocyanine, 381
- L**
 Labarc, 80, 161
Lachesis lanceolatus, toxin, 691
 Lacquers, 410, 585, 591
 accelerated weathering tests, 586, 587, 590
 chlorinated rubber, 611, 612
 nitrocellulose, 562, 576, 580, 587
 Lactalbumin, 839-841
 Lactation, effects of irradiation, 836
 Lactic acid, 436, 448-450, 540, 672, 742, 752, 753, 764
 acrylic ester, polymer, 456
 phenyl, 477, 478, 540
 Lactic aldehyde, 518
 Lactoflavin, 563, 848, 851, 852
 Lactose, 432, 433, 435, 521, 711
 nitrobenzylidene acetal, 472
 Lakes, 590, 643
 Lambert's law, 206
 Laminated glass, 411
 Lamphack, 583, 659
 Lamps (see also Mercury arc)
 antimony, 148
 bismuth, 148
 bulbular, 132
 cadmium, 148-150
 cathode-ray bombardment, 152, 156
 dental, 141
 fluorescent, 142, 152
 for black light, 179
 for exciting luminous paints, 583
 gaseous conduction, 132
 glow, 132, 138-141
 incandescent, 152
 lead, 148
 Mazda CX, 143
 mercury discharge, 131-142
 metal vapor, deterioration, 150
 Osram, 68, 175, 539, 640
 Philips, 139
 positive column, 132, 139
 selenium, 148
 Sollux, 580
 sun, 111, 129, 134, 141, 143-146, 561, 738, 887
 tellurium, 148
 therapy, 97, 132-134, 138, 139
 tubular, 132
 tungsten, 156, 173
 Uviol, 108, 114, 182
 xenon, 151, 300, 308, 393
 zinc, 148-150
 Lanolin, 563, 743, 792, 813
 Lanthanum compounds, 142
 Lard, 556, 559, 789
 Larvac, 718, 765, 766
 Latent image, 373, 374, 376-381
 Latex, 593, 594, 596, 597
 Lattice, crystal, 372-374, 385
 Lauth's violet, 263, 631
 Lavender oil, 513
 Lead, 150, 172, 464, 661
 and fatty acids, 554
 driers, 572, 573
 excretion, 760, 825
 glass, 165
 ion, 377
 lamp, 158
 poisoning, 825
 reduction scale, pigment, 583
 seals, for mercury arc, 74, 75, 80
 sols, 386
 spark, 155
 Lead abietate, 558
 acetate, 184, 613, 616, 726
 arsenite, 358, 359
 carbonates, 577, 583
 chromates, 391, 608, 615, 616
 hydroxide, 386
 oxide, 168, 360, 481, 630
 peroxide, 253, 341
 phthalate, 481
 picrate, 354
 tetraethyl, 464, 657
 tetramethyl, photolysis, 464
 tetraphenyl, photolysis, 464
 Leather, 293, 645, 650, 651
 Leaves, plant, 498, 715, 866, 886
 Lecithin, 669, 750, 766, 834
 Leg weakness, 202, 782, 786, 787, 813, 814
 Lemon juice, reducing agent, 849
 oil, 513
 Lens, of eye, 164, 762-764
 Lentil seeds, 716, 885
 Lepidine, 508, 521
 Lethal action, of ultraviolet rays, 193, 247, 692-707, 716
 Lettuce, irradiated, 830, 889
 Leucine, 671
 Leucobases, of triphenylmethane dyes, 627, 628
 Leucocytes, 746-748, 751, 756, 759
 Leucomethylene blue, 263, 264, 630, 631
 Levulinic acid, light absorption, 451
 Levulose, 432, 433
 Leyden jars, 149, 154, 292
 Licanic acid, 574
 Liebermann's polyester, 484
 Liesegang rings, 391, 392
 Light, as inhibitor of reactions, 255
 as limiting factor in photosynthesis, 873
 complex, additivity of effects, 442
 nature of, 2, 3, 4, 6
 polarized, 4, 435, 442, 882
 Light-fastness of dyes, 634-642
 Lighting, fluorescent, 142
 Light-stroke, 860
 Lignin, 550, 617, 620
Limax flavus, embryos, 718
 Lime, 168, 169, 171, 172, 179
 Lime blossoms, 657
 Linen, 188, 205, 615, 618, 620, 645, 646
 Limes, Balmer, 156, 163
 enhanced, 32, 33
 forbidden, 92
 intensities and origins, 106
 intercombination, 29
 mercury, 65, 67, 92, 115, 116, 188
 physical isolation, 189, 190
 resonance, 136, 137, 141, 150, 151
 reversed, 109, 110, 152
 spectral, width of, 243
 Linoleic acid, 553, 554, 558, 564, 567
 Linolenic acid, 553, 554, 567, 570
 Linoleum, 573, 574, 727
 Linolic acid, 570
 Linseed oil, 557, 565, 613, 650
 absorption spectrum, 555, 568-571
 and lithopone blackening, 386
 bleaching, 568, 573
 bromination, 567-569
 drying, 567-570, 572, 574
 in sterilization, 727
 irradiated, 789
 oxidation, 558, 559, 569
 products from, 573
 Lipase, 680, 683, 742, 756
 Lipid phosphorus, in cancer tissue, 766
 Lipids, 669, 670, 727, 883, 887
 Lipochrome, 559
 Lipoid peroxide, in plant photosynthesis, 876
 Liquids, photoreactions in, 335-336
 Litharge, in rubber, 610
 Lithion carmine, 634
 Lithium bromide, 239, 344
 carbonate, 172

- Lithium chloride, 390, 681
 fluoride, prisms, 7
 halides, 239
 iodide, 239, 372, 373
 nitrate, 479
 Lithographic inks, testing, 641
 Lithol red, barium salt, 643
 Lithopones, 575, 590, 600, 743
 actinometer, 104, 105
 and vulcanization, 599
 blackening, 384-386, 580
 in rubber, 610
 light absorption, 582, 583
 paints, accelerated tests, 577, 580
 photoconductivity, 385
 Liver, beef, antirachitic substance, 817
 calcification, 820
 catalase, 685, 756
 extracts, 630, 686
 glycogen, 753
 inorganic phosphorus, 818
 of irradiated animals, 789
 oil, absorption spectrum, 854
 oxygen consumption, 825, 826
 Locke's glass, 174, 175
 Lovibond scale, 165, 642
 Lubricating oil, 557, 652, 653
 Lumichrome, 851, 852
 Lumiflavin, 851, 853
 Luminescence, 265, 375, 559
 analysis (see Fluorescence analysis)
 Lumisterol, 807-812, 816
 Lupus, 742, 769
 Lyman region, 7
 series, 21, 22
 Lymph, 751
 Lymphocytosis, 746
 Lymphoid tissue, 759
 Lymphopenia, 746
 Lysin, 759
 Lysine, liberation of ammonia, 672, 677
 Lysis, of irradiated cells, 704
M
 Mace oil, absorption spectrum, 513
 Macronuclei, 703
Macrosporium tomato, 711
 Madder lakes, 590
 Magenta, 634, 642
 Magnalium mirror, in discharge tube, 142
 Magnesia, 168, 360, 582, 583
 Magnesium, 171, 760
 Magnesium carbonate, 176, 583, 609, 868, 869, 878
 chloride, 361, 704
 discharge lamps, 141, 142
 flashes, 290
 glass, 170
 hydroxyazonaphthalenedisulfonate, 502
 in blood, 754
 in plants, 889
 lines, temperature classification, 26
 nitronaphthalenesulfonic acid, 502
 of skin, 742
 peroxide, 573
 phosphates, 172
 resinates, 585
 spark, 795, 797-799, 801, 808, 816, 834
 sulfate, 440, 890
 underwater spark, 155
 Magnetic susceptibility, 294
 Mahua oil, oxidation, 559
 Maize oil, 560, 563
 Malachite green, 265, 350, 498, 592, 595, 627-629, 634, 639, 868, 869
 Malaria, 776
 Maleic acid, 211, 407, 412, 452-454, 455, 457, 541, 621
 anhydride, 453, 806, 834
 Maleonitrile, 457
 Malic acid, 361, 445, 518, 660, 672, 764, 884, 891
 Malonic acid, 440, 441, 447, 523
 anhydride, 447
 Malpighian layer, of skin, 734, 735
 Malt-agar medium, irradiation, 708
 Malt, 681, 682, 722
 Maltase, 681
 Maltoflavin, 851
 Maltose, 432-434, 436
 Mammary glands, irradiation, 754
 Mandelic acid, 448-450, 481, 540
 Manganese, abietate, 558
 and cotton, 617
 and fatty acids, 554
 and lithopone blackening, 385
 cations, absorption spectra, 337
 chloride, 434, 456, 545, 870
 complex cyanide, 363
 driers, 572
 in carbon arc, 57
 in glass, 168, 176
 in plants, 889
 lines, temperature classification, 26
 oxides, 165-167, 171, 176, 863
 salts, 187, 353, 370, 409, 498, 727
 sulfate, 364
 Manganic hydroxide, 363
 Manila resin, 585
 Mannitol, 383, 403, 472
 Mannose, 432, 472, 883
 Margarine, 556
 Marine organisms, irradiation of, 717, 718
 Mass, action and photochemistry, 206
 reduced, 224
 spectrograph, 227
 Mastitis, 777
 Material, seldedge-resistant, 621
 ultraviolet-transmitting, 172-176
 Maxwell-Boltzmann law, 245
 Mazda lamps, 143, 889
 Mead, aging, 660
 Meadow-lane, transmission by, 188
 Meal worm chrysalids, 744
 Mean critical tone, of dyes, 635
 Meat industry, ultraviolet radiation in, 724
 Mechanism, of photochemical processes, 205-216
 Media, bacteriologic, 694, 695, 698, 712, 716
 Medicinal products, sterilization, 725-728
 Meesmaecker reaction, 796
 Melanin, 671, 684, 739, 740, 890
 formation, 671, 684
 Melanoblasts, 671
 Meleostose, hydrolysis, 435
 Mellon Institute, air pollution studies at, 98
 Membranes, collodion-lecithin, 669
 formation by eggs, 717
 Menhaden oil, diving, 574
 Meningococcus, 696
 Menthol, and acetone, 514
 Menthyl derivatives, 404, 453, 743
 Mercaptans, 463, 654
 Mercaptides, in petroleum products, 652
 Mercaptobenzothiazole, 600, 605
 Mercerization, 616
 Mercuric acetate, 541
 bromide, 455
 chloride, 205, 267, 366, 367, 371, 444, 445, 705
 iodide, 367, 391, 812
 nitrate, 364
 oxide, 302, 367, 371, 502, 630, 883
 sulfate, 439
 sulfide, 384, 391
 Mercurochrome, 658
 Mercurous bromide, 105
 chloride, 105
 iodide, 399
 nitrate, 455
 sulfate, 367
 Mercury arc, abnormal, 82
 absorption by mercury within, 107, 109, 110, 115, 117, 118, 121, 124, 132, 136, 141, 144
 accessories, 81
 alternating current operation, 91, 92
 aging, 100, 102, 104, 117, 127-130
 anode processes in, 81, 85
 anodes, 73, 74, 80
 as polariscope source, 68
 as radiation standard, 99, 100
 carbon anode, 74
 cathode processes in, 32, 79, 81-83, 93
 cleanup of mercury in, 84

- Mercury arc, commercial, 72, 78
 constricted, 64, 65, 68, 84, 87, 88, 115, 119-124, 129, 130, 190
 Cooper-Hewitt, 100, 107-114, 131, 143, 150, 158, 693, 789
 deposits in, 129, 130
 distribution of mercury in, 73, 75, 78-80, 84
 effect of arc current, 84, 106, 108, 114, 115-117
 effect on glass, 175, 176
 effects of irradiation by, 615, 650, 681, 682, 694, 696, 701, 731, 734, 744, 745, 748, 770, 778, 779, 784, 787, 824
 effect of pressure on, 77, 84
 effect of temperature on, 86-89, 117
 electrical characteristics, 79, 81, 84-90
 electrodes, 73, 74, 80, 133, 137
 electromagnetic deflection of, 118, 119, 122
 explosion of, 124
 Fischer, 69
 for 3650 Å., 179
 for forming ozone, 68, 69, 292, 293
 for photochemistry, 68-73
 General Electric Vapor Lamp Co., 131
 green line, 177, 178
 Hanovia, 79, 129
 Heraeus, 78, 147
 high pressure, 68, 72, 78, 80, 81, 84
 history of, 65, 66
 Hulburt, 72
 instability, 77, 87-90
 iron anode, 69, 75
 K B B., 104
 Kromayer, 57, 126, 127, 735, 744, 769, 770, 797
 Labarc, 80, 161
 laboratory-built, 68-72
 leads, 74, 75, 78-80
 low pressure, 80, 81, 86, 87
 measurement of line intensities, 103
 molybdenum in, 79, 80, 83
 operated on lighting circuit, 75
 pole vessels, 79
 pressure in, 77, 79, 80, 84, 87, 94
 Pyrex windows, 72
 radiating fins, 73, 79
 regulation, 88-90
 resistance for, 81
 R.U.V., 107
 seals, 72, 74, 75, 80
 spectral energy distribution, 74, 77, 78, 87, 94-97, 106-117, 141, 157, 195
 starting, 68, 69, 73, 74-77, 79, 91, 92
 strengthening, 78
 temperature of electrodes, 73, 74, 78, 80
 theory, 81-95
 tungsten anode, 79, 80
 uses, biological, 71-73, 81, 771
 uses, industrial, 578, 580, 581, 607, 618, 635, 636, 638-640, 643, 656, 719, 720, 723, 799
 Uviarc, 80, 81, 85-87, 89, 92, 100, 117, 129, 134-137, 174, 175
 variation of output after striking, 116, 117
 Victor, 701
 water-cooled, 73, 78, 80, 86-89, 124-127
 Weigert, 71
 Mercury-argon discharge, for milk irradiation, 840
 Mercury, attempted conversion to gold, 366
 cathode, irradiated, 339
 compounds, 142, 268, 367
 dimethyl, photolysis, 464
 discharge lamps, 131-142, 654, 655, 723, 842
 effect on sulfur dioxide photolysis, 330
 emission bands, 92, 94, 95
 energy-level diagram, 27-29, 92
 excited, 93, 231, 257, 258, 295, 302
 formation, 464
 fluorescence quenching, 257
 fulminate, 367, 463
 glow discharge, 93
 halides, 367
 hydride bands in S-1 sunlamp, 144
 interrupter, 154
 ionization potential, 27
 isotopes, 227
 lines, 28, 92, 93, 144, 146
 metastable, 92, 93, 257, 258, 322
 Mercury, molecule, 95
 nitrate, 353
 oxide, and cholesterol, 812
 phthalate, 481
 purification, 124
 reaction with methyl iodide, 399
 resonance lines, 8, 27, 29, 92, 117-124, 127, 257, 800, 829
 sensitization by, 257, 258, 301, 304, 305, 466
 sulfides, 367
 toxicity, 124
 -vapor arc, 65-97
 Mesaconic acid, methyl, 456
 Mesidine, 647
 Mesitylene, oxidation, 468
 Mesityl oxide, 429, 461, 494
 Mesophyll, in irradiated plants, 715
 Metabolism, basal, 744-746, 825, 826
 carbohydrate, 751-753
 Metal carbonyls, 464
 Metaldehyde, 418
 Metals, and fatty acids, 554
 and ergosterol, 832
 and lacquer yellowing, 592
 and lithopone blackening, 384, 385
 and stability of trinitrotoluene, 472
 bonding with rubber, 611
 corrosion, 661
 deposition, 359
 irradiated, 563, 728
 in liquid ammonia, photoreaction, 349
 in plant photosynthesis, 878
 oxides, 58, 472
 particles, in preservative wrappers, 562
 salts, as photosensitizers, 862
 sols, preparation, 386, 387
 vapor arcs, non-mercury, 147-151
 Metastable state, mercury, 92, 93
 Metastases, of sarcoma, 766
 Metastylene, 488
 Metatungstic acid, 369
 Meter, ultraviolet, 97-100
 Methacrylates, polymerization, 584
 Methane, absorption spectrum, 393, 394
 chlorination, 395, 526-529, 532, 533
 chlorine-sensitized oxidation, 394, 395
 decomposition by sparks, 45
 diiodo, 400
 effect on ethyl diazoacetate photolysis, 460
 formation, 258, 394, 396-398, 407, 416, 418, 420, 425, 427, 428, 431-433, 438, 448, 458, 459, 461, 464, 480
 photolysis, 240, 391
 reaction with acetylene, 415
 reaction with iodine chloride, 280
 sensitized reaction with deuterium, 394
 Methanol, 433, 439, 455, 533, 882
 absorption spectrum, 401, 402
 formation, 397, 433
 oxidation, 402, 404
 photolysis, 231, 402
 removal of metal carbonyls, 464
 Methemoglobin, 680, 863
 Methoxyaniline, 497, 498
 Methoxybenzophenone, 477
 Methoxybenzylacrylic esters, 491
 Methoxycinnamic acid, 483, 487
 Methoxycinnamylidenecetic acid, 485
 Methoxyethoxycarbonyl aldehyde, nitration product, 476
 Methoxymethylphthalate, 592
 Methoxyl group, effect on coumaric acid transformation, 488
 Methoxyquinoline, 521
 Methoxy, phenylfluorene thioglycolic acid, 511
 Methyl acetate, and sulfite oxidation, 356
 Methylacetylene, polymerization, 415
 Methylacrylonitrile, polymerization, 457
 Methylal, 397, 416
 Methyl alcohol (see Methanol)
 Methylalloxazine, 852
 Methylamine, 322, 408, 458, 522, 523, 883
 2-Methyl-5-aminopyridine, 520
 Methylanisylacrylic acid, 491
 Methylanthracene, 505, 509

- Methylanthrahydroquinol carboxylic lactone, 507
 Methylanthraquinones, 506, 617
 Methylarbutin, 436
 Methylazoxybenzene, 496
 Methyl benzalpyruvate, 491, 492
 Methyl benzoate, 340, 480
 Methylbenzophenone, 477
 Methylbenzoylacrylate, 491, 492
 3-Methyl-6,7-benzoylene-benzopyrrole, 518
 Methyl-4-benzylidene-3-methylhydantoin-1-acetate, 518
 Methylbenzyl oxide, 595
 Methyl bromide, 395, 396
 Methyl bromo-5-bromo-2,4-dimethoxybenzoylacrylate, 491
 Methylbutyl ketone, 421, 429
 Methylchalcone, 490
 Methyl chloride, 394-396, 526-529, 532
 Methyl chloroformate, 539
 Methyl chloromethylsulfate, formation, 538
 Methylcholanthrene, 765
 Methyl cholate, 670, 817
 Methylcinnamide, 484
 Methylcoumaric acid, 488
 Methyl cyanide, dissociation, 231
 Methylcyclohexanone, 516
 Methylcyclopentanone, 516
 4-Methyl-2,6-dianisal-1-cyclohexanone, 517
 Methylidihydrochalcone, semicarbazone, 491
 Methyl diphenylmaleate, 454
 Methylene aminoacetoneitrile, 612
 Methylene blue, 182, 259, 265, 599, 629-631, 633, 686
 and chlorophyll, 873
 and irradiated skin, 742
 and oxidation of oils, 558
 and plasma oxidation, 678
 and rubber gelation, 595
 and textiles, 614, 617
 and vaccine virus, 712, 713
 bleaching, 263, 630, 640
 filter, 744
 in actinometry, 102, 103, 105
 oxidation of mandelic acid, 449, 450, 481
 reduction by ascorbic acid, 849
 reduction by milk, 761, 762
 reduction by pyruvic acid, 451
 sensitizer, 498, 862
 -succinic acid reaction, 447
 Methylene chloride, 394-396, 528
 Methylene dioxychalcone, 490
 Methylene dioxy-syn-aldoxime, 494
 Methylene green, actinometer, 105
 iodide, 398, 399
 radicals, 430
 Methylene-*p*-toluidine, 610
 Methylene violet, 265, 629
 Methyleneethylenecarbinol, 404
 Methyleneethylene, formation, 429
 Methyleneethyl ketone, 421, 429
 Methyl formate, 439, 539
 Methylfluorene, 490
 Methyl fumarate, 455
 Methylgalactose, nitrobenzylidene acetal, 472
 Methyl halides, 440
 2-Methyl-3-hydroxy-4,5-di(hydroxymethyl)-pyridine, 850
 Methylindigo, 616
 Methylindole, 517
 Methyl iodide, 244, 246, 395-399
 Methylisatin, 616
 9-Methylisalloxazine, 852
 Methylisobutyl ketone, 494
 Methylisopropylacetaldehyde, 809
 Methyl- γ -ketopentadienedicarboxylate, 489
 Methyl laurate, oxidation, 559
 Methyl maleate, 455
 Methyl mercuric iodide, formation, 399
 Methylmesaconic acid, 456
 Methyl methacrylate, 584, 596
 Methyl (4-methylphenyl) (*p*-ethylphenyl)trimethylmethane, 267
 Methylnaphthaquinone, 502
 Methylnaphthoxazole, 743
 Methylnaphthopyrone, 502, 503
 Methylnaphthoyl chloride, 549
 Methyl nitrite, photolysis, 460, 461
 o-Methyl-3-nitro-4-methoxybenzaloxime, 494
 Methyl-*o*-nitro-*o*-methoxycinnamate, 483
 o-Methyl-6-nitro-3,4-methylenedioxybenzaloxime, 494
 Methyl orange, 382, 622, 868
 Methyl oxalate, 340
 Methylphenazonium salts, 522
 Methyl phenoxybenzoylacrylate, 491
 10-Methyl-9-phenylanthracene, photooxide, 508
 Methylphenylglyoxime, 461
 Methylphenylindone, 493, 517
 Methylphenyltetrachloroarsine, 549
 2-Methyl-1,3-propane diol, 833
 Methylpropyl ketone, formation, 429
 Methylpyridines, 519
 Methylpyridones, 261
 Methylpyridinium salt of 1,8-nitronaphthalenesulfonic acid, 502
 Methyl radical, 393, 397, 398, 417, 420, 421, 427-430, 438, 459, 460, 464, 529
 Methyl red, chlorophyll-sensitized reduction, 625, 626
 Methyl salicylate, 481
 Methyl stearate, 541
 Methylstyryl ketone, semicarbazone, 494
 Methyl sulfate, 538
 Methyl truxillate, 484
 Methyl violet, 179, 259, 260, 634, 639, 640
 Methylumbelliferone, 621
 Methyluracil, 698
 Mica, filters, 188, 694
 Mice, sensitization to light, 751, 860
 Micelles, silver, 383
 Michler's ketone, 477, 629
 diethylmercaptol, 626
 Microscope, fluorescence, 651, 665
 Migration, electrophoretic, 387, 388
 in *N*-substituted amines, 496, 497
 of O atom from nitro group, 471, 472, 474-476, 516
 Milk, and methylene blue, 761, 762
 antienzymes, 840
 destruction of vitamins of, 848, 854
 flavin assay, 852
 film capacity, 841, 844, 846
 flavor, 563, 829
 irradiation, 721, 761, 785, 789, 793, 827, 829, 831, 835-846
 oxidation-reduction potentials, 761, 762, 849
 protection from light, 563
 provitamin content, 841
 secretion, 761, 785, 836
 sterilization, 721, 722
 xanthine oxidase of, 686
 Millimicron, 5
 Mineral oil, 555, 600, 610, 619, 651, 652, 727, 743, 789
 rubber, 610
 Minerals, fluorescence, 178, 664
 spark spectra, 42
 Mint tablets, accelerated testing, 513
 Mirror test, atomic hydrogen, 429, 438, 439
 Mitogenetic rays, 101, 150, 767, 768
 Mitosis, distribution of nucleic acid, 704
 Mohair, fluorescence, 645
 Moisture, and Budde effect, 282
 and cotton deterioration, 614
 and textiles, 613
 effect on hydrogen-oxygen combination, 299
 Molds, irradiation, 659, 694, 711, 723, 724, 828, 831, 838
 Molecular electrolysis, 259, 260, 339
 Molecular orientation, and photoreactions, 265
 spectra, 217, 228, 230, 231, 234, 235
 Molecules, antisymmetrical, 226
 Molecules, diatomic, band spectra, 218-223, 230
 excited, 212, 214, 216, 218, 226, 229, 242, 251, 262, 264
 heteropolar, 221, 237, 240
 homopolar, 221, 222, 224, 226-240
 polyatomic, 231, 241, 244
 symmetrical, 221, 226
 "Moleoxides," of oils, 558

- Molybdenum, 58, 74, 79, 80, 83, 149, 369
 chlorides, 545
 oxides, 152, 244, 354
 spark, 154
 "Molybdenum indigo," 244
 Molybdic acid sol, 369
 Moment of inertia, 222, 225, 227
Monarda fistulosa, essential oil, 513
 Monoalkylmalonic acids, 447
 Monobromobenzene, 543
 Monobromomethylanthraquinones, 506
 Monobromophenylcyclopropane-1,2-dicarboxylic acid, 541
 Monobromopinacolone, 539
 Monobutyrin, 436
 Monochloroacetic acid, 104, 401, 451, 452, 540, 594
 Monochlorococleole, 550
 Monochlorohexamethylene, 531
 Monochlorohydrocarbons, 531
 Monochloroisooheptane, 530, 531
 Monochloromethane, 529
 Monochloromethylanthraquinone, 506
 Monochloropinacolone, 538, 539
 Monochromators, 96, 190, 696, 782, 800, 808
 Monodehydrochlorophyll, 878
 Moniodopentachlorobenzene, 544
 Monomolecular films, proteins, 676, 677
 Mononitromethylanthraquinones, 506
 Montan wax, in rubber, 610
 Mordant, copper compounds, 645
 dyes, fading, 635, 642
 Morphine, 525, 726, 741
 Mosquito larvae, 765
 Mother-of-pearl, 165
 Mt. Wilson, solar energy at, 199
 Muconic acid, 484
 Multiplicity, in spectral series, 24, 25
 of molecular states, 225, 226
 Multiplets, 24
 "Multiple-hit-to-kill" relation, 705, 707, 708
 Muscle, 753, 760, 761, 818, 820, 862
 Mushroom, irradiated, 831
 Mustard, 886
 Mustard oil, 513, 559
 Mutarotation, and circularly polarized light, 435
 Mycelia, of fungi, 711, 889
 Mylius reaction, 670
N
 Nainsook, 189
Naja tripudians, toxin, 691
 Nakagawa reaction, of bile acids, 669
 Naphthacenes, 509-511
 Naphthadanthrone, dimethoxy, 507
 Naphtha dyes, 643
 Naphthalene, 183, 414, 469, 471, 501-503, 507, 508, 549, 591
 β -Naphthaleneazo- β -naphthol, 503
 Naphthalene, azoxy, 493
 blue, 634
 chloro, 549
 diamino, 497
 1,5-dibenzoyl-2,6-dimethyl, 549
 Naphthalene, 1,5-di-(*o*-chlorobenzoyl), 549
 diazonium chloride, 625
 nitro derivatives, 501
 β -tetrachloro- α -keto, 493
 tetrahydro, 613
 Naphthoquinones, 502
 Naphthenes, 655
 Naphthionic acid, 382
 Naphthobianthrone, 506
 Naphthol, 469, 471, 646, 659, 863
 acyl derivatives, 647
 dyes, 634
 Green, 632, 634
 sulfonic acids, 382, 390, 643, 743
 Yellow, 643
 Naphthophenazine, 626
 Naphthoquinone, 507, 603
 Naphthoxazole, methyl, 743
 Naphthoyl chloride, 2-methyl, 549
 Naphthylaldehyde-1-carboxylic acid, 549
 Naphthylamine, 382, 497, 515, 519, 575, 646
 Naphthylamine sulfonic acids, 382
 Naphthylaminocamphor, 268, 515
 Naphthyliminocamphor, 516
 Narcotics, and plant photosynthesis, 875, 876
 Narcotine, 849
 Natural gas, chlorination, 526-528
 Natural Green, 638
 Naval powders, 462
 Necrobiotic rays, 768
 Negative branch, 223
 Negative glow, 30, 31, 132, 138-140
 Nencki's hematopoiphysin, 751
 Neoparsphenamine, 759, 776
 Neocyanine, 381
 Neodymium oxide, 19, 178
 Neolan Green, 640, 642
 Neon, 27, 136, 138, 144
 Neon-argon discharge tube, 722
 Neoplasms, 766
 Neoprene, fluorescence, 601
 Neirst glower, 34
 Nerves, 733, 862
 Nervous control, effects of irradiation, 734, 740, 746
 Neutral red, 631
 New Brunswick, solar energy at, 195
 "Newglass," 175
 New Orleans, solar radiation at, 202
 Newsprint, 619
 Nickel, 166, 168, 169, 334, 415
 cations, absorption spectra, 337
 electrodes, 131, 138, 160, 161
 in cored-carbon arc, 55
 leads for mercury arc, 78, 79
 lines, 26, 238
 rods, 148
 salts, 187, 359, 370, 409
 sensitizer, 265, 354, 554, 617, 832
 spark, 154
 Nickel carbonate, 268, 869, 870
 carbonvils, 331, 333, 334, 465
 chloride, 187
 hydroxide, 368
 oxide, 132, 179, 368, 663, 685, 870
 sulfate, 186, 359
 Nicol prism, 270
 Nicotine, 521-523, 883
Nicotinea glutinosa, 712
 Nicotinic acid, 523, 703, 850
 Night blindness, 858
 Nigrosin, 634
 Nile blue, 264, 498, 631, 634
 Ninhydrin, and wool, 622
 Nitra lamp, 580, 703
 Nitraniline, 497, 558
 Nitrate ion, electron-affinity spectrum, 337
 photolysis, 211
 reduction, 102, 104, 259, 353, 354
 Nitrates, 102, 171, 193, 322, 350-353, 523, 883
 Nitrations, 469, 470
 Nitre, 165
 Nitric acid, 193, 351, 352, 407, 469, 479, 518
 Nitric oxide, absorption spectrum, 160, 324, 325, 326
 and aldehyde photolysis, 421, 422
 and dyes, 633
 effect on various photolyses, 326, 327, 460, 464
 formation, 51, 304, 351, 364, 461, 462, 475
 inhibitor of hydrogen-chlorine combination, 285
 photoionization threshold, 269
 photolysis, 325, 326
 reaction with carbon monoxide, 310
 reaction with cyanogen, 58
 Nitrides, 58, 139
 Nitriles, 458
 Nitrites, absorption spectrum, 351, 461
 and formaldehyde, 882
 and hydrogen peroxide photolysis, 341
 formation, 259, 322, 350, 352, 458, 523, 869, 883
 in atmosphere, 193
 in soil, 350, 351
 Nitroamine cobalt compounds, 368
 Nitroamines, and textiles, 499
 2-Nitro-4-amino- α -naphthol-7-sulfonic acid, 643
 Nitroamine cobaltic chloride, hydrolysis, 368
 Nitroanilines, 495, 519

- Nitroanisole, 592
 Nitroanthracene sulfonic acids, 502
 Nitroanthraquinonesulfonic acids, 506
 Nitrobenzaldehyde, 472, 474-476
 Nitrobenzaldoximes, methyl ether, 493, 494
 Nitrobenzalpentaerythrito-1-spiran, 516
 Nitrobenzene, 188, 467, 482, 496, 510, 592
 Nitrobenzenedisulfide, 501
 Nitrobenzenesulfonic acids, 501
 Nitrobenzodimethylamidoxime, 494
 α - β -Nitrobenzyl ethers, of aldioximes, 494
 Nitrobenzylidene acetals, 472
 α -Nitrobenzylideneglycols, 472
 Nitrobromostyrene, 489
 Nitrocamphor, 515
 Nitrocellulose, 354, 462, 463, 588
 films, 585, 588, 589, 650
 lacquer, 562, 576, 580, 583, 587
 photolysis, 589, 592
 Nitrochalcones, 490
 Nitrocinnamaldehyde, 475
 Nitrocinnamic acid, 482
 Nitrocobaltic compounds, 260
 Nitro compounds, 460-463, 469-472
 2-Nitro-4',4''-diaminotriphenylmethane, 626
 Nitrodimeylaniline, 497
 4-Nitro-2,6-dinitrosodihydroxymethylbenzene, 471
 Nitro dyes, 640, 643
 Nitrogen, 144, 156, 279, 345, 422, 468, 470, 471, 523, 650
 absorption, 181, 193, 317
 active, 37
 and anthraquinone, coloration, 506
 and dyes, 626, 633
 and egg albumin, 678
 and hydrogen, 318
 and insulin irradiation, 679
 and peptides, 674
 and phosphoride, 879
 and rubber, 593, 595, 601, 602
 compounds, photochemistry, 317-329
 discharge in, 137, 139
 effect on chlorination of acetylene, 537
 effects on various photoreactions, 296-298, 305, 309, 316, 318, 321, 327-329, 331, 358, 400, 401, 426, 428, 435, 436, 460, 462, 475, 537, 545
 fixation in soil, 350, 351
 for irradiation, 184
 for lamps, 583
 formation, 64, 351, 384, 456-462, 498, 500, 515, 624, 625
 glow discharge, 30, 31
 heat of dissociation, 235
 in gasoline testing, 653, 654
 in metal-vapor lamps, 150
 ionization potentials, 27
 isotopes, 227
 metabolism, 745, 746
 organic compounds and light-fastness of pigments, 575
 oxidation, 324
 photoionization threshold, 237, 269
 predissociation, 242
 resonance potentials, 27
 Nitrogen dioxide, 247, 327, 371
 iodide, 354
 oxides, 193, 194, 240, 324-328, 733
 pentoxide, 210, 327, 328, 354
 peroxide, 304, 324, 457, 469, 470, 521
 predissociation, 241, 243, 244, 326, 327
 trichloride, 285, 329
 trioxide, 515
 Nitroglycerin, 354, 461, 462
 Nitro group, 488, 516
 Nitromethoxybenzaldoximes, 494
 5-Nitro-2-methoxy-3-ethoxybenzaldehyde, 476
 Nitromethylnaphthalene, 502, 549
 Nitronaphthalene, derivatives, 501, 502, 549
 Nitro-nitroso-hydroxymethyl-benzoquinone-oximes, 471
 Nitroparaffins, 461
 Nitrophthalide, 548
 Nitrophthalaldehydic acid, 548
 Nitrophenols, 499
 Nitrophenylethyl ketone, 478
 Nitropiperonal, 515
 Nitro-rayon, 613
 Nitrosobenzaldehyde, 475
 Nitrosobenzene, 469, 470, 496
 Nitrosobenzoic acid, 472, 474, 475, 516
 Nitroso compounds, oxidation, 461
 Nitrosodimethylamine, 382
 Nitrosodimethylaniline, 178, 179, 182, 495, 497
 Nitrosodimethylhexane, 461
 Nitroso dyes, 640
 Nitrosoisopropyl acetone, 461
 Nitro-naphthylhydroxylamine, 503
 Nitrosoterephthalaldehydic acid, 476
 Nitrosulfonic acid, 546
 Nitroterephthaldehyde, 476
 2-Nitro-3,4,2',5'-tetramethoxy- α -phenylcinnamic acid, 484
 Nitrotoluenes, 467, 469, 472, 496, 502
 Nitrotriphenylmethane, 626
 Nitrous acid, 351, 498
 organisms, of soil, 351
 oxide, 285, 324, 325, 327, 397, 461, 462, 633
 Nitrosyl chloride, 328, 329, 460, 470
Nitzschia closterium, 790
 Nonachlorocyclohexane, 543
 Nonex glass, 75
 Northrop-Kunitz electrophoresis cells, 704
Nostoc, 883
 Novarsenol, 776
 "Noviol," 165, 180, 187, 188, 886
 Novarsolan, 776
 "Noviweld," 165
 Novocaine, 740
 Nuclei, formation in air, 387
 Nucleic acids, 690, 696, 698, 700-703, 712, 716, 850
 Nuclein phosphorus, 766
 Nucleins, irradiated, 703
 Nucleoproteins, 696, 712
 Nucleus, of cell and lethal action, 696
 Number, atomic, 21
 quantum, 21, 22
 Nursing mothers, irradiation, 785
- O**ak bark, extract, 743
 Oats, 886, 887
 Octachlorobutane, formation, 401
 Octachlorocyclohexene, 543
 Octane, formation, 394
 Octoic acid, 559
 Octyl alcohols, 658
 Octylaldehyde, absorption spectrum, 416
 Oil, almond, 743, 513
 bergamot, and sunburn, 743
 cacao, 556
 cade, 513
 candlenut, 574
 cassia, 513
 castor (see Castor oil)
 Chinawood, 564-567
 cinnamon, 513
 clove, 513
 cocoanut, oxidation, 559
 cod-liver (see Cod-liver oil)
 cola, 559, 612
 corn, 557, 574
 cottonseed (see Cottonseed oil)
 dogfish, 853
 eucalyptus, bleaching, 513
 fish-liver, 555, 853
 lavender, 513
 linseed, 555, 557, 565, 613 (see also Linseed oil)
 lemon, absorption spectrum, 513
 mace, 513
 Mahua, oxidation, 559
 maize, 560, 563
 menhaden, drying, 574
 mineral (see Mineral oil)
 Monarda fistulosa, 513
 mustard, 513, 559
 oiticica, 574
 olive (see Olive oil)

- Oil, palm, 556, 610
 peanut (see Peanut oil)
 peppermint, 513
 perilla, 567, 571, 573, 574
 petroleum, 651
 pilchard, 574
 pine, 610, 659
 plant, activated, 815
 poppyseed, 567, 571, 572, 574
 rat liver, 854
 Red S, 610
 rubberseed, 574
 sassafras, 513
 sesame, 559
 shale, 865
 shark-liver, 855
 solar, chlorination, 531
 Soluble Red O, 659
 soybean (see Soybean oil)
 sunflower, 571, 574, 790
Telfairia, 574
 thyme, 513
 transformer, 561
 taubaki, 559
 tung (see Tung oil)
 Turkey red, 613
 turpentine, 513, 514, 610
 vegetable, 555, 557, 610, 612, 789
 whale, 555, 557
 wintergreen, 513
 wormseed, 513
- Oils, aging, 589
 drying, 205, 531, 564-574
 essential, 513, 727, 728
 fluorescence, 555, 556, 600
 formation in plants, 882
 hydrogenation, 558
 irradiation, 727, 728, 827
 lubricating, 557
 oxidation, 558, 572
 polymerization, 564-566
 sensitizing ultraviolet photography, 381, 556
 staining fabrics, 624
 stereoisomeric changes, 564-569
 unsaturated, detection, 558
- Ointments, sterilization, 727
- Optical activity, and photochemistry, 266-268
- Optimum wave-length for lethal action, 701, 706, 714
- Oranges, killing molds on, 711
- Orange II, 625, 532
- Orbital quantum numbers, 226
- Orbits, electronic in atoms, 21-23
- Orders of spectra, 33
- Organic acids, 184, 186, 361, 362, 540
 dyes, detection, 575
- Organizer, embryonic, 765
- Organometallic compounds, 464, 465
- Ortho hydrogen, 226
- Ortho-para hydrogen conversion, 244
- Orthostannic acid, 366
- Oscillator, molecular, 220, 223, 224, 232-235
- Oscillatory circuit, for starting mercury arc, 92
- Oscillograph, cathode-ray, 271
- Osmundia (lavtoniana)*, 890
- Osram lamp, 68, 175, 539, 640
- Ostwald color system, 581
- Ova, roundworm, 718
- Overall photochemical reactions, 245-256
- Ovoflavin, 852
- Ovooverdin, 859
- Oxalates, 267, 441-445
- Oxalic acid, 205, 469, 503
 absorption spectrum, 441
 actinometer, 202
- Oxalic acid, and aniline, 495
 and ferric salts, 361
 and pinene, 515
 bromine reaction, 447
 chlorination, 541
 effect on manganioxalate photolysis, 442
 formation, 405, 451, 467, 470, 480, 484, 514, 869
 in photosynthesis, 867
 in tobacco plant, 884
 iodine reaction, after-effect, 447
 oxidation, 251, 252, 350, 366, 441, 443, 448
 photolysis, 103-105, 246, 440, 441, 443-447
 reaction with hydrogen iodide, 249
- Oxalyl chloride, 448
- Oxanthrol, 508
- Oxanthrone, 508
- Oxazine dyes, 640
- Oxen, light sensitization, 861
- Oxidase, 671, 742, 749, 756
- Oximes, 410, 493, 494
- 4-Oxo-9,10,11,12,13,14-octadecatrienylcarboxylic acid, 574
- Oxyacetylene flame, 35
- Oxycellulose, 614, 615, 617, 618
- Oxygen, 192, 279, 345, 348, 359, 370, 407, 457, 467, 468, 471, 479, 649
 absorption spectrum, 179, 181, 193, 194, 249, 293-295
 active, 292, 349, 468, 727, 728, 864
 and biological photosensitization, 862, 863, 864
 and chlorophyll, 871, 872, 877
 and fluorescence quenching, 262-264, 864
 and plant photosynthesis, 876-880
 and polymerizations, 410, 489, 584, 595
 and rubber, 595, 596, 601
 and textiles, 615, 621, 626
 and vitamin D production, 797, 798, 804, 806, 807
 as free radical, 295
 atomic, 251, 252, 304, 475
 excited, 293, 296, 297, 300, 309
 reactions, 300, 302, 309
 combination with nitrogen, 324
 dissociation, 293, 294, 300, 309
 effect on acetone fluorescence, 426
 effect on photohalogenations, 529, 532-535, 537, 540-542, 545, 546
 effect on hydrogen-chlorine combination, 281, 283, 285, 287-289, 302
 effect on nitrogen peroxide fluorescence, 327
 effect on oxidation of lactic acid, 448
 efforts on various photolyses, 296, 297, 315, 327-330, 332, 367, 377, 397, 400, 417, 442, 444, 460, 462, 515, 853
 electrical conductivity, 473, 514
 equilibrium between O_2 and O_4 , 294, 295
 evolution from photooxides, 508-511
 excitation, 243
 excited molecules, 294, 295, 300
 filter, 309
 formation, 64, 305-307, 346-348, 352, 475
 heat of dissociation, 235, 243, 293, 294, 354
 in accelerated paint tests, 578, 579
 in gasoline testing, 653-655
 in milk irradiation, 840, 841
 in plant cells, 874
 inhibitor of phosgene formation, 311-314
 ion, 264
 isotopes, 227
 liberation by plants, 866
 magnetic susceptibility, 294, 295
 metastable, 264
 migration from nitro group, 516
 predissociation, 293, 300
 purification, 510
 transformation to ozone, 292-295
- Oxygenase, 889
- Oxyhemoglobin, 750
- (Oxy)hydrogen flame, 35
- "Oxy" acids, 564
- 2-Oxyquinoxaline-3-aldehyde, 851
- Oxytocic hormone, pituitary, 689
- Ozone, 345, 350, 401, 411, 413, 556, 568, 625, 650, 727, 733, 788

- Ozone, absorption of ultraviolet rays, 7, 193, 194, 295-297
 and dyes, 633, 634, 638, 640
 and hydrogen peroxide, 339
 and insulin, 679
 and isoeugenol, 514
 and paper, 619
 and pyridine, 519
 and rubber, 597, 598, 602, 603, 606
 and vitamins, 804, 840, 848
 bleaching by, 618
 excited molecules, 296
 formation, 292-295, 299-300, 309
 in accelerated paint tests, 579
 in atmosphere, 193
 in food irradiation, 828, 829
 in laundries, 727
 in vitamin D production, 832
 inhibitor of Eder reaction, 445
 photolysis, 211, 259, 292, 295-298
 toxicity, 293
 Ozonides, 410, 415, 728
- P** branch, 223, 225
 Paintings, fluorescence, 663
 Paints, accelerated tests, 575-581
 bleaching, 575, 576
 chlorinated rubber, 611
 drying tests, 574
 films, 572, 577-579
 for rubber, 610
 luminous, 583
 outdoor exposure tests, 578, 581
 reflecting properties, 583
 stable to ultraviolet rays, 183
 ultraviolet-reflecting, 583
 Palatinol, 589
 Palisade cells, in irradiated plants, 715
 Palladium, 159, 161
 Palm oil, 556, 610
 pitch, in ebionite, 608
 Palmitates, 586
 Pancreas, secretory activity, 760
 Pancreatic diastase, 681
 Pancreatin, 681, 682
 Papaveraldine, 520, 521
 Papaverine, 520, 521
 Paper, 561, 619, 625, 644
 bleaching, 617, 618, 644
 deterioration, 618-620
 dyed, 643, 644
 fluorescence tests, 620, 644, 663
 light-sensitive, 363, 384
 pH, 644
 photographic, 363, 383, 384, 647, 648
 pulp, yellowing, 618
 rolls, removing electric charges from, 662
 testing, 641
 ultraviolet penetration, 619
 ultraviolet reflection, 618, 619
 water resistance, 620
 yellowing, 562
 Papillomas, 766
 Paracetaldehyde, 422
 Paraldehyde, 418, 613
 Paracyanogen, 456
 Paraffin oil, 508
 Paraffins, 531, 533, 607, 610, 651-653, 661
 Paraformaldehyde, 460
 Para hydrogen, 226, 274, 290, 317, 397, 402, 420, 439, 811
 Paramagnetic ions, and fluorescence quenching, 263
 Paramecia, lethal action on, 523, 696, 700, 701, 703, 716, 717, 752, 860, 865
 Paraquinone, and rubber oxidation, 603
 Parathyroids, 755, 790, 819
 Parathyroidectomy, 749, 755
 Paratoluidine, reaction with crotonic acid, 456
 Para toners, 590
 Parazone, 604
 Parchment, 561, 562
 Particles, in atmosphere, 194
 Pasadena, solar energy at, 199
 Paschen series, 20, 22, 163
Pasteurella infection, 776
 Patent leather, 293, 572, 650
 Pauli exclusion principle, 25
 Pauly test, wool, 623
 Peaches, composition, 891
 Peanut oil, 559, 743, 790, 795, 828
 Pears, composition, 891
 Peas, 886, 889
 Pelargonic acid, 559
Pelargonium leaves, 715, 872, 873
 Pellagra-preventing factor, photolysis, 850
 Pentachlorobenzene, 543
 Pentachlorocyclohexane carboxylic acid, 547
 Pentachloroethane, 401, 535
 Pentacyanoaquoferrate, 362, 363
 Pentacyanoaquoferrite, 362
 Pentadiene, tetraphenyl, 411
 Pentahydroxyamylbenzimidazole, 851
 Pentane, 394, 526, 527, 529, 531
 Pentathionic acid, 354, 390
 Pentene, isomerization, 413
 Pentosans, 883
 Pentoses, 435
 Pentyl chloride, 531
 Pentylene, 394
 Peppermint oil, 513
 Pepsin, 247, 680, 683, 890
 Peptides, 676, 677
 Peptones, 411, 674
 Peracetic acid, 422, 484
 Peracid, furu, 517
 Peracids, 422, 880
 Peraldehyde, 880
 Perbenzoic acid, 473
 Perborates, 410, 657
 Percarbonates, 410, 657
 Perchlorates, 298, 307, 341, 346, 348, 349, 455
 Perchloroethylene, 657
 Performic acid, 440
 Perfructose, 433
 Perithecia, of fungi, 890
 Perilla oil, 567, 571, 573, 574
 Periodates, 348
 Periodic reactions, 256
 Permanent Red 4B, lake, 643
 Permeability, of erythrocytes, 750, 752
 of membranes and irradiation, 669
 Peroxidase, 685, 686, 742, 889
 Peroxides, 433, 440, 473, 481, 561
 and oleic acid, 553
 and polymerizations, 584
 and vitamin D, 804
 formation, 403, 422, 467, 468, 653, 654, 656, 812
 in alcohol irradiation, 402, 404
 in ether, 405
 in irradiated oils, 727, 728
 in photodynamic action, 863
 in plant photosynthesis, 876, 881
 in rubber oxidation, 604
 mono and di-alkyl, 339
 of dyes, 633
 of fats and oils, 558-560, 572
 of linoleic acid, 553
 of porphyrin, 680
 of rubrene derivatives, 509-511
 organic, 383, 407, 411
 Per salts, 411
 Perseulose, 432
 Persulfate ion, 355
 Petylene, 512, 595
 "Peter Pan" gingham, 642
 Petrolatum, 652, 727
 Petroleum products, 530, 531, 651-657
 Phenanthrene, 504, 508, 511, 550, 591
 Phenanthrenequinone, 482, 603
 Phenazines, 497, 498, 522
 Phenetidine, 497
 Phenols, 356, 390, 469, 479, 499, 500, 562, 573, 631, 648, 657, 833
 acyl derivatives, 647, 648
 amino, 468, 496, 497
 and aldehydes, 584
 and chlorophyll bleaching, 871
 and insulin, 679

- Phenols, and nitrocellulose, 463
and rubber oxidation, 603
as fluorescence quenchers, 262
chloronitroso, 479
dinitro, 499
fluorescence, 600
galactoside, 680
glucoside, 680
homologs, esters, 547
inhibitors, 340, 410, 445, 474
oxidation, 863
mannoside, 680
nitro, 499
resins, 410, 584, 585, 592, 611
vinyl derivatives, 411
- Phenolase, 742
- Phenolphthalein, 259, 629
- Phenosafuranine, 260, 264, 498, 631
- Phenoxybenzoylacrylic acid, 491
- Phenylacetaldehyde, 424, 473
- Phenylacetic acid, 477, 478
- Phenylacetylene, iodination, 538
- Phenylacridine, 509
- Phenylalanine, 670, 671, 696, 739
- Phenylanthracene, 508, 509
- Phenylazobenzene, 575
- Phenyl benzoate, 480
- 4-Phenylbenzohydrol, 477
- 4-Phenylbenzophenone, 477
- Phenyl bromide, 544
- 2-Phenyl-1,3-butadiene sulfone, 413
- Phenyl-10-carboxyanthracene, 508
- Phenyl chloride, 543
- Phenylcinnamic acid, bromination, 487
- Phenylcinnamitrile, 485, 488, 743
- Phenylcinnamylidenecetonitrile, 484
- Phenyldiazonium chlorides, 500
- Phenyldibenzoxanthrenium dyes, 647
- Phenylenediamine, 260, 495, 498, 575, 646
- Phenylethyl chloride, 546
- Phenylethylene, 488
- Phenylethylindane, 811
- Phenylfluorenes, 512
- Phenylfluorenylcarbinols, 512
- Phenyl fluoride, 544
- Phenylglyoxal osazone, 450
- Phenylglyoxime, 461
- Phenylphenatrienic acid, 492
- Phenylhydrazine, 183, 450, 478, 498, 575, 614, 625, 626, 630
- Phenylhydroxylamine, 470, 496
- Phenylhydroxystyryl ketones, 493
- Phenylindole, 743
- 9-Phenyl-10-iodoanthracene, 508
- Phenyl iodide, 644
- Phenylmethyl carbinol, 403
- Phenylmethyl ketone, 540
- 3-Phenyl-2-methylindone, 492
- Phenylmethyl ketone, 595
- 2-Phenyl-6-methylquinoline, 521
- Phenylmorpholines, 612
- Phenyl- α -naphthylamine, 604
- Phenyl- α -naphthyl ketone, 477
- Phenyl- β -phenylstyryl ketone, semicarbazone, 494
- β -Phenyl- β' -phenyltruxone, 517
- Phenylpropionic acid, 541
- Phenyltriazolines, 478
- Phenylquinoline, 743
- Phenylquinoline carboxylic acids, 521
- Phenyl radical, 472
- Phenylsemicarbazone, 495
- 2-Phenyl-5-styryl-6-nitroisatogen, 471
- Phenylurethane, 875, 877
- Phenylvinylacetic acid, 413
- Phenylrhodide-*b*, fluorescence, 879
- Phaeophytin, 764
- Phloroglucinol, 479, 630, 648
- Phloxin, 264
- Phosgene, 227, 311
decomposition, 314-317
formation, 310-314, 346, 394, 400, 448, 460, 532-535
- Phosphatase, 683, 754, 785, 818, 819, 822
- Phosphate glass, 132, 133, 172, 176
- Phosphates, 681, 784, 785, 818, 828
- Phosphatides, 670, 791
- Phosphine, 332, 333, 359
- Phosphite, 370
- Phosphorescence, 262, 264, 265, 375, 385, 665
- Phosphoric acid, 369, 669, 710, 753
- Phosphorus, 64, 141, 358, 596, 778
absorption, 745
and rickets, 779, 783-786, 818, 820, 830
chlorides, 64, 545
conversion of yellow to red, 359, 596, 598
in blood, 774, 778, 783-785, 788, 822
in plants, 888, 889
nitride, 218, 219
pentoxide, 168, 179
red, 332, 540
- Photoanisotropy, 266, 283
induced, 383
- Photocellulose, 614
- Photochemical processes, theories of mechanism, 205-216
- Photochemistry, early work, 205
- Photocolorimeter, 636
- Photoconductivity, 269, 380
- Photodichroism, 266, 857
- Photodynamic actions, 260, 261, 860, 861, 865
- Photoelectric cells, 97, 99, 100, 107, 271, 771
effect, 17, 214, 269, 375, 505, 732, 733, 877
- Photoelectrons, liberated by x-rays, 209
- Photoequivalence law, 207, 210-213
- Photofluorescein, 864, 865
- Photographic desensitizers, 863
papers, 255, 647, 648
plates, 180, 209, 271
processes, non-silver, 365, 384, 481, 485
- Photography, chromated gelatin, 365
- Photoionization, 269
- Photoisopropylcalciferol, 810
- Photometers, 105, 107, 161, 270
- Photon, 10, 18
- Photonitrication, 351
- Photoxides, of hydrocarbons, 508-510
- Photoprocesses, in crystals, 372-376
in liquid and gas phases compared, 335, 336
- Photopyridine, 433, 519, 520, 646
- Photopyrocalfiferol, 810
- Photosphere, 191
- Photronic cells, 96, 97
- Photosantonic acid, 516
- Photosensitizations, 257-269, 336, 380, 381, 510, 741, 745, 860, 862-864
- Photosensitizers, 257, 862
- Photostationary states, 274, 504
- Photosynthesis of carbohydrates, 873-882
- Photosynthetic units, 881
- Phototropy, 371
- Phototropy, 268, 481, 489, 493-495, 516, 521
- Photovoltaic effects, 269, 464
- Phthalanil, 592
- Phthalaldehyde acid, 548
- Phthalan dyes, 629
- Phthalic acid, 469, 481, 507, 617
- Phthalic anhydride, 617
- Phthalic esters of hydroquinone ethers, 591
- Phthalide, 548
- Phthalimide, 550, 592
- Phthiocol, 502
- Phycocerythrin, 881
- Phylloporphyrin, 861
- Phylloerythrin, 872
- Phytin, and fermentation, 710
- Phytoplankton, 790
- Phytosterol, 791, 872
- Picea excelsa*, 873
- Picein, 162, 436
- Pickering lines, 33
- Picoline, 518
- Picolinic acid, 518, 520
- Picramic acid, 498
- Picric acid, 101, 354, 472, 498, 499, 598
- Pigmentation of fruits, 870, 891
of human skin, 734, 739, 740, 772, 773
- Pigments, 575, 581-583, 589, 590, 608, 609
fading, 205
formation in bacteria, 888
fluorescence analysis, 575

- Pigments, on mustard, 886
 Pigs, 746, 786
 Pilchard oil, 574
 Pilocarpine, 522
 Pimpinellin, 515
 Pinachrome, 632
 Pinacolone, 538, 539
 Pinacols, 477, 514, 517, 816
 Pinacone, 404
 Pinacryptol, 264, 265, 498, 863
 Pinacyanol, 334, 381, 465
 Pinaverdol, 632, 871
 Pine bark extract, 167, 563
 oil, 610, 657, 659
 pitch, 610
 Pinenes, 210, 473, 514, 515
Pinus strobus, 873
 Piperidine derivatives, 425, 466, 525, 598
 Piperitone, 515
 von Pirquet test, 775
Pisum, seedlings, 888
 Pitch, 662
 Pittsburgh, solar radiation at, 201
 Pituitary, oxytocic hormone, 689
 Pityriasis rosea, 769
 Placental hormones, 689
 Planck's constant, 8, 10, 18, 207
 Plants, ash, 889
 coumarin formation, 487
 development, 58, 150, 205, 886-888
 diseases, 890
 lethal action on, 715, 886
 oils, activated, 815
 respiration, 889
 Plasteins, 674
 Plaster of Paris, 768
 Plastics, 410, 411
 Plasticizers, 173, 409, 589, 590, 612, 650
 Platonic acid, 248, 369, 370
 Platinum, 74, 131, 253, 339, 364, 369, 415
 catalyst, 341, 439, 454
 sol, 386, 388, 390
 "Plexiglas," 172
 Plums, composition, 891
 Pneumococcus, 776, 824
 Polarized light, 266-268, 348, 353, 368, 383, 698, 882
 Pole-caps, for therapy lamp, 133, 134
 Pole-vessels, mercury arc, 79
 "Pollopas," 165
 Polyatomic molecules, 223, 224, 236, 240, 241, 244
 Polycarboxylic acids, 481
 Polychlorohydrocarbons, 531
 Polychromatic light, photoreactions by, 254, 255
 Polyglycolide, 451
 Polymerization, 406, 408-411, 557, 564-567
 Polymers, benzaldehyde, 511
 bivinylyl, 411
 from isopropenylmethyl ketone, 429
 of acrylic esters, 584
 vinyl esters, 410
 Polyneuritis, 851
 Polyphenols, antioxidants, 610
 Polysaccharides, 869
 Polystyrenes, 488
 Polyvinyl chloride, 411
 Ponceau R G, 636, 637, 640, 642
 Pongee, 188
 Poppyseed oil, 571, 572, 574
 Pork production, and sunlight, 785
 Porphyrins, 261, 263, 553, 685, 687, 751, 767, 860, 861
 Porphyrinuria, 861
 Porphyropsin, 859
 Positive branch, 223
 Potash, 166, 171
 Potassium acetate, 183
 acid phthalate, 185
 alum, 612
 amalgam, 360
 amide, 349, 350
 and muscle, 760
 anthraquinone sulfonates, 506
 antimonyl tartrate, 450
 arsenic tartrate, 450
 Potassium bichromate, 620
 bismuth tartrate, 450
 bisulfate, 357
 borotartrate, 450
 bromide, 383, 433, 434, 450, 538, 540, 681
 carbonate, 176, 869
 chlorate, 348, 495
 chloride, 141, 183, 383, 434, 681, 704
 chromate, 179, 187, 364, 522
 cobalticyanide, 363
 cobaltioxalate, 441, 442
 copper tartrate, 450
 cuprioxalate, 442
 cyanide, 265, 363, 439, 480, 627, 629, 812, 861
 dichromate, 187, 336, 344, 364, 365, 404, 439
 469, 612, 629, 646
 ferricyanide, 363, 495, 646
 ferrioxalate, 442, 443
 ferrocyanide, 362, 363, 405, 631
 fluoride, 141, 440
 formate, 344, 345
 hydrogen phthalate, 187
 hydrogen phosphate, 684
 hydroxide, 185, 358, 362, 508
 iodate, 345
 iodide, 187, 433, 434, 446, 541, 629, 680, 681
 and metabolism, 745, 759
 crystals, 372, 373
 oxidation, 251, 260, 343, 344, 348, 371, 381
 photolysis, 104, 247, 342, 343, 370
 in blood, 754
 ion, 682, 761
 iron tartrate, 450
 manganioxalate, 267, 442
 mercuric oxalate, 444
 nitrate, 102, 104, 176, 498, 681, 800, 883
 photolysis, 348, 352, 353
 nitrite, 255, 351, 352, 882
 of skin, 742
 oleate, 553
 oxide, 168
 oxalate, 254, 344, 345, 442, 445-447
 palmitate, 553
 permanganate, 252, 364, 371, 452, 614
 persulfate, 209, 251, 357, 358, 371
 sulfate, 358, 390
 stearate, 553
 tellurate, 384
 thiocyanate, 358, 675
 Potato chips, rancidity, 561
 tubers, solanine content, 890
 Potential energy curves, 163, 229, 232-236, 239
 241, 242, 374, 375, 453
 Potentials, ionization, 27
 oxidation-reduction, 433
 resonance, 27
 sparking, 40
 Poultry (see Chicks)
 Powders, gun, 462
 Precipitins, 759
 Predissociation, 214, 235, 241-244, 263
 Preen glands, 787
 Preserves, sterilization, 722
 Primary process, photochemical, 207, 211-214, 216
 227, 229-245, 336
 Principal series, 23, 24
 Prints, 479, 622
 Prism, 4, 6, 190
 Probes, 31, 48
 Prolan, 689
 Proline, 676, 703
 Propanes, 258, 394, 396, 429, 526, 531, 532, 546
 550, 612
 chlorinated, 532, 534
 Propanol, 404, 538
 Propene, 429
 Propenylmethyl ketone, 429
 Propionaldehyde, 244, 397, 404, 416, 421, 425
 hexahydrophenyl, 424, 473
 Propionanilide, 438
 Propionic acid, 404, 437, 438, 441, 540
 Propiolic acid, phenyl, 541
 Propiophenone sulfonic acid, 413
 Propyl alcohol (see Propanol)
 bromide, isomerization, 399

- Propyl ethylene, 429
 disulfide, and gasoline, 654
 iodide, photolysis, 396, 398
 radical, 429
 Propylene, 396, 407, 422, 534
 Provitamin D, 792
 Prussian blue, 341, 362-364, 390
 Protective glasses, 164-167
 wrappers for foods, 560-563
 "Protectoid," 165
 Proteinases, 683, 684
 Proteins, 181, 411, 674-680, 696, 701, 705, 716,
 717, 739, 740, 873
 blood, 756, 863
 denaturation, 365, 675, 676
 disintegrated, 753, 773
 fluorescence, 735
 in antibodies, 758, 759
 irradiated and gold sols, 669
 light absorption, 670
 metabolism, 745
 of lens, 763
 of lymph, 751
 of retina, 858
 oxidation, 671, 863
 photosynthesis, 882, 883, 887
 protective action on pepsin, 684
 reaction in surfaces, 265
 shock, 734, 773
 Protease, 677
 Prothrombin, 684
 Protochlorophyll, 888
 Protoplasm, 767
 Protozoa, lethal action on, 247, 701, 716, 717
 Pseudobutylene, 407, 408
 Pseudocumene, 469, 550
 Pseudocumidine, 647
 Pseudoglobulin, 677
 Pseudonitric acid, 352
 Psoriasis, 769
Pteris longifolia, 890
Puccinia spores, 711
 Pulfrich step photometer, 581, 636
Pulmonaria leaves, 715
 Pulp, wood, 618, 645
 Pump, Gaede, 148
 Punicic acid, 566
 Purines, 698, 700, 701, 703, 746, 850, 851, 863
 Purple bacteria, photosynthesis by, 881
 Pustular folliculitis, 769
 Pyocyanine, 522
 Pyran derivative, 268
 Pyrazole, formation, 460
 Yellow, 632
 Pyrazolines, 1-phenyl, 478
 Pyrazolone dyes, 640
 Pyrene compounds, 183, 562
 Pyrethrum, toxicity, 658, 659
 Pyrex, 72, 75, 103, 146
 Pyridine and derivatives, 356, 407, 433, 518 521,
 613, 687, 703
 Pyridinium bromide, hexadecyl, 644
 Pyridinium 1-nitronaphthalene-8-sulfonate, 502
 Pyridones, *N*-methyl, 261
 Pyridoxine, 850
 Pyrimidines, 698-703, 850, 851
 Pyrocatechol, 807, 810-812
 Pyrocatechol, 469, 509
 Pyrogallol, 260, 410, 475, 631, 688
 Pyroxylin, 562, 591
 Pyrrole, derivatives, 466, 518
 Pyrrolidines, formation, 407
 Pyruvic acid, 421, 449, 451, 518, 630, 702
 Pyruvic dehydrogenase, 687
- Q** branch, 223, 225
 Quanta, for carbohydrate photosynthesis, 866
 required to kill a bacterium, 705, 706
 values at various wave-lengths, 207
 Quantum, of action, 8
 mechanics, 25, 26, 217, 236, 372, 374, 375, 453
 numbers, 21-25, 220-223, 226
 theory, 10, 11, 17, 18, 21, 22, 206, 218-226
- Quantum yield, 102, 104, 105, 210-213, 247, 248,
 251, 252, 336, 373
 fumaric-maleic interconversions, 453, 454
 hydrogen-chlorine combination, 289-291
 hydrogen iodide photolysis, 272
 in plant photosynthesis, 874-876, 879-881
 in lethal irradiations, 705
 milk irradiation, 844
 ozone photolysis, 296, 297
 Quartz, 7, 74, 151, 165, 169, 172-175
 "Quartzlite," 170, 173-175, 181, 185
 Quebracho extract, 563
 Quercetin, 621
 Quinaldine, 522, 592
 Quinic acid, monoacyl derivatives, 523
 Quinidine sulfate, 523
 Quinine, 206, 210, 340, 523-525, 658, 664
 bichloride, 522
 bisulfate, 441, 522, 743
 sulfate, 183, 252, 347, 356, 500, 523, 562, 640,
 657
 Quininic acid, 521
 Quinol, 469, 726
 Quinoline derivatives, 521, 743
 dyes, 640
 Quinones, 101, 474, 479-481, 507, 596, 622, 679,
 871
 Quinotoxin, 523
 Quinoxaline, 851
 Quinonoximes, 471
- R** branch, 223, 225
 Rabbits, oxygen consumption, 744
 Racemization, 512
 Radiation, continuous for absorption measurements,
 152-163
 emission mechanism, 11, 15-29
 erythema-producing, 100, 101
 infrared, 2, 6
 lethal, 100, 101, 143, 193
 measurement of, 96, 97, 100
 mitogenetic, 101, 150, 767, 768
 necrobiotic, 768
 processes, stellar, 191, 192
 resonance, 190
 solar, ultraviolet in, 1, 2, 142, 191
 synergy of wave-lengths, 442, 443, 486
 tan-producing, 57
 theory of reactions, 209, 210
 ultraviolet, nature of, 2, 6, 7
 visible, nature of, 2, 3, 4, 6
 Radiationless transitions, 242
 Radicals, free, 231, 244, 864
 Radioactive emanations, and petroleum products,
 655
 Radiomalt, 832
 Radiotoxic spectral sensitivity, 714
 thresholds, 714
 virulence, 714
 Radium, 467, 683, 686, 733
 Raffinose, 435, 890
 Rag papers, 620, 644
 Raman effect, filters for, 188
 source for, 137, 138, 149
 spectra, 213, 222, 224, 593, 665
 of gasolines, 665
 of rubber, 593
Rana pipiens, 766
 Rancidity, 558, 559, 560, 562, 563
 Rapid Filter Yellow, 632
 Rare earths, 19, 166, 261, 369, 370
 Rates, photochemical reaction, 207, 245, 246, 251-
 253
 Rays, 188, 613, 619-621
 Rays (see Radiations)
 Reactance, in starting mercury arc, 76
 Reactions, chain, 213-215
 overall photochemical, 245-256
 Realgar, 359
 Reciprocity law, 101, 271
 Recombination, of atoms, 231, 253, 279, 280, 335
 Rectifier, for starting a.c. mercury arc, 92
 Red algae, photosynthesis, 881
 Red blood cells (see Erythrocytes).

- Red lead, 577, 583
 Red oil, 557
 Reduced mass, 236
 Reduction potentials, of dyes, 531
 Reflectance, of skin, 738
 Reflectors, 771, 844
 Refraction, 4
 Regenerated cellulose, 184, 619
 Reichert-Meissl number, 837
 Reindel's isoergosterol, 796, 797
 Rennet, 247, 684
 Rennin, 658
 Rentschler meter, 201, 202
 Resins, 410, 411, 584, 585, 589, 592, 610, 619, 655, 663
 Resinate, 585, 612
 Resonance, 262, 263
 lines, 37, 92, 117-119, 121, 124, 127, 136, 137, 141, 150, 151, 190, 257
 potentials, 8, 26, 27
 Resorcinol, 469, 630, 688
 Resorcinolazobenzene, 562
 Respiration, 687, 863, 867, 874, 877, 889
 of plants, 889
 Respiratory center, 753
 enzymes, 687, 688, 891
 quotient, 746
 Reticulocytes, 748, 749
 Retina, 164, 687, 733, 762, 857, 858
 Retinene, 858
 Reversed lines, underwater spark, 152
 Reversing layer, sun, 192
 Revertex, 611
 Rhamnose, 432, 472
 Rhinitis, 776
 Rhodamine, 142, 188, 260, 383, 451, 585, 620, 634, 639
 Rhodium, 74
Rhodovibrio, 707
 Ribbons, sterilization, 727
 Rice, 685
 Ricin, 690
 Ricinoleic acid, 554
Ricinus communis seeds, 683
 Rickets, 143, 174, 733, 738, 778, 779, 781-785, 827, 862
 Ringer's solution, irradiated, 761
 Road tar, accelerated weathering test, 661
 Rochelle salt, reaction with bromine, 252
 Rock salt, 372, 373
 Rods, of retina, 857
 Root storage, 887
 Rose Bengal, 264, 634, 863
 Rosin, 557, 585, 586, 610, 619, 620, 644
 Rosindulin, leucobase, 678
 Rosindulines, formation, 517
 Rotational energy levels, 218, 220, 222, 229
 Rotenone, 659
 Rubber, accelerated weathering tests, 562, 605-609
 bonding, 611
 cements, gelatin, 597
 chlorinated, 611, 612
 composition, soles, 608
 curing, 598
 fluorescence, 601
 oxidation, 601-605
 plants, 890
 polymerization, 429, 593-597, 601, 602
 preservation, 609, 610
 Raman spectrum, 593
 reclaimed, 607
 soles, 593-595
 stretched, X-ray diagram, 593
 substitutes, 411, 558, 573, 612
 surface films, 599
 synthetic, 593
 Rubbersed oil, 574
 Rubene, tetraphenyl, 509
 Rubidium, 238
 Rubidium iodide, 238
 Rubrene derivatives, 509-511, 603, 864
 Ruhmkorff coil, 76
 Russell effect, 383, 556, 790
 Ruthenium hydroxide, 370
 γ -pentacarbonyl, 370
 Rydberg constant, 32
 formula, 20, 22, 23
 Rye, germinating, 885
S
Saccharomyces, (see Yeast)
 Safe-T-Aire equipment, 729
 Safety glass, 411, 588, 591
 Safranin, 260, 585, 630, 634, 639
 St. John's wort, 861
 Salicin, 436
 Salicylaldehyde, 423, 476, 481
 Salicylanilic acid, ultraviolet sensitizer for plates, 381, 382
 Salicylic acid, 478, 481, 548, 725, 741
 Salivary diastase, 681, 682
 Salkowsky reaction, 623
Salmo lacustris, embryos, 765
Sal. typhimurium, 706
 Salol, 562
 Salvia plants, minerals in, 889
 "Santalum," 173
 Sanocrysin, 744
 Santonin, 516
 Saponin, 382, 436, 824
 Sarcoma, 766, 828
 Sassafras oil, 513
 Sawdust, irradiated, 788
 Scandium lines, 26
 Scarlet HR, 647
 Scatole, 517
 Schenectady, solar energy at, 197, 198
 Schüler cathodes, 151
 Schütz law, 681
 Schumann plates, 7, 381
 region, 7, 8, 208, 231, 241, 293, 300
 -Runge bands, 293-295
 Schwarzschild law, 271
 Scleroderma, 742
Sclerotium bataticola, 711
 Scleroderma, 769
 Scurvy, 849
 Sea urchin eggs, 764
 Secondary photochemical processes, 211, 212, 214, 216, 245, 248, 250, 253, 254, 335
 Secretin, 689
 Sector, rotating, 254, 270, 446, 447, 486, 875
 Sedimentation, red blood cells, 756
 Seedlings, 715, 885, 886
 Seeds, 887, 890
 Selection principles, 24, 25, 220, 222, 225, 226, 243
 Selective irradiation, 726, 828
 Selenides, 142
 Selenious acid, 384, 514
 Selenium, 148, 269, 358, 384
 chlorides, 545
 oxides, 360, 431
 red, 598, 599
 Selenomercaptan, and gum formation in gasolines, 656
 Self-extinction, 263
 Self-inductance coil, 41, 42
 Self-reversal, 65
 of mercury lines, 65, 109, 110
 Semiacetals, 437
 Semicarbazones, 490, 491, 494, 495
 Semi-cbonites, fluorescence, 601
 Semicumones, 263
 Sensitivity, photographic, theories, 378, 379
 Sensitization (see Photosensitization)
 Separation of lines by refraction, 189, 190
 Sericin, 622
 Series, spectral, 23, 24, 163
 Serine, 672
 Serum albumin, 674-678, 862
 amylase, 756
 and pancreatin, 682
 antitryptic activity, 757
 calcium, 754, 784 (see also Calcium, in blood)
 cholesterol, 755, 825
 globulin, 675-677, 706
 index of refraction, 756
 inorganic phosphorus, 710, 754
 irradiated, 674, 675, 677, 706, 751, 753, 756, 758, 863

- Serum albumin, "kallicrein," 691
 opsonina, 757
 protective action on venom, 691
 reducing power, 710
 surface tension, 756
 vasoconstricting power, 746, 747
- Sesame oil, 559
- Shale oil, 865
- Shark-liver oil, 855
- Sharp series, 23, 24
- Shaving creams, sterilization, 727
- Sheep, 861
- Shellac, white, 382
- Shock, 733
- Siak-illipe nut, sterols, 792
- Silane, 333
- Silent discharge, 292, 310
- Silica, 165, 166, 168-172, 179, 189, 583
 gel, 264, 391, 392
- Silicates, in carbon arc, 58
- Silicon carbide, 51
 oxychloride, 288, 289
 tetrachloride, 64
 tetrafluoride, 51
- Silk, 188, 613, 620-622, 642, 674
 artificial, 188, 613, 616, 620, 621
 dye-fading, 502, 622, 637, 639
- Silkworm eggs, catalase, 685
- Siloxene, 333
- Silver, 97, 150, 231, 378, 380, 398, 415, 463
 acetate, 438
 acetylde-gelatin emulsion, 384
 azide-gelatin emulsion, 384
 bromide, 240, 373, 376-378, 380, 381, 599
 chloride, 6, 240, 349, 376, 377, 383
 chromate-gelatin gels, 391
 filters, 150, 178, 762
 halides, 237, 240, 376-380, 383
 iodide, 239, 240, 376, 378
 nitrate, 260, 364, 439, 726
 and cholesterol, 812
 gelatin gels, 391
 preparation of silver sols, 387
 reaction with zinc oxide, 371
 reduction, 159, 383, 384
 oxalate, 384, 441
 oxides, 371, 410, 508
 salts, 205, 359, 371, 384, 645
 sols, 386-390
 sulfide, 379
 thioarsenite, 389
- Sinapis alba*, nitrogen content, 884
- Sipalin, 576, 650
- Sitosterols, 792
 7-dehydro, 811, 816, 817
- Sizes, for cloth or paper, 411
- Skin, 669, 678, 684, 713, 733-744
 absorption of vitamin D, 847
 active oxygen in, 727
 and parathyroids, 755
 and typhoid immunization, 757
 cholesterol, 766, 791
 cream, irradiated, 847
 fluorescence, 651
 glutathione, 751
 grafting, 770
 infections, 774, 775
 lipase, 756
 proteinase, 756
 provitamin, 705, 814, 816
 respiration, 826
 senile, 769
 substance affecting castrated mice, 756
 sugar, 751
 tumors, and irradiation, 511, 742, 766, 865
 vitamin C content, 849
 wounds, 825
- Sky Blue, 639
- Skyshine, 198-202, 782, 828
- Smoke, in air, 196, 201, 202
- Smokeless powders, 462
- Snail lipins, 792
- Snake venom, 691
- Soaps, 555, 556, 563, 582, 648, 741, 847
- Sockets, after tooth extraction, 769
- Soda, 171
- Sodium, 27, 131, 141, 231, 238, 257, 360, 373, 674
 acetate, 183, 434, 437
 alcoholate, 476
 alizarine sulfonate, 646
 amide, 349, 350
 anthraquinone sulfonates, 449, 506, 682
 azide, 354, 363, 481
 benzoate, 185
 3-benzoyl-aminopyrenedisulfonate, 562
 bicarbonate, 354, 450
 bromide, 567
 carbonate, 450
 chlorate, 347, 646
 chloride, 183, 373, 375, 433, 675, 681, 704, 763
 chlorite, 347
 2-chloroanthraquinone-6-sulfonate, 506
 chlorocinnamate, 483
 N-chloro-p-toluenesulfonamide, 265
 cinnamate, 187
 cholate, 670
 chromate, 364
 cyanide, 354, 749, 750
 dichloroanthracenedisulfonate, 682
 dichromate, 407, 408, 502, 616
 fluorescein, 864
 fluoride, 172, 681
 formate, reaction with iodine, 252, 440
 fumarate, 452
 glycocholate, 670
 glycol, 411
 hydrosulfite, 358, 463, 507
 hydroxide, 187, 450, 508
 hypochlorite, 346, 347, 589
 hypophosphite, 370
 hyposulfite, 616
 iodide, 231, 237, 238, 342, 344, 372, 373
 ketyl radical, 477
 lactate, 449
 maleate, 452
 molybdate, 369, 383, 619
 naphthionate, 503, 631
 nitrate, 440, 498, 646, 681, 883
 nitrite, 249, 344, 345, 351, 371, 377, 439
 nitroferrocyanide, 363
 nitroprusside, 341, 363, 364
 nucleate, 703
 peroxide, 573
 6-phenyl-2-aminopseudoaziminobenzenedisulfonate, 648
 phenylbenzimidazolesulfonate, 743
 phenyldiazosulfonate, 645
 7-phenylheptatrienic acid, 492
 phosphates, 172, 370, 640
 pyrenetetrasulfonate, 562
 oleate, 391, 555
 oxide, 168, 179
 resinate, 619
 salicylate, 481
 selenite, 817
 silicate, 763
 stannate, 619
 sulfate, 340, 341, 691
 sulfide, 495
 sulfite, 356, 357, 410, 450, 863
 tartrate, 450
 thiocyanate, 358
 thiosulfate, 358, 598
 toluenesulfonchloroamide, 498
 triiodomethanesulfonate, 400
 tungstate, 383, 387
 "Soft-lite," 166
- Soil, 350, 351, 391
- Solanine, formation in potatoes, 890
- Solar constant, 1, 2
 energy distribution, 7, 142, 191, 192, 195-202
 oil, 531, 653
- Solarium arcs, 62, 63
- Solarization, 173-176
- Solio paper, 640
- Sollux lamp, 580
- Sol-rubber, 593, 594
- Solvates, 437
- Solvation, 249, 335-337

- Sorbitol, 433, 472
 Sorbose, 432, 867
 Sound records, 662
 Sources, continuous for absorption studies, 152-163
 dual purpose, 142-147
 illuminating, 15
 of radiations, survey, 30-37
 standardization by oxalic acid photolysis, 443
 Soybean oil, 557, 559, 567, 573, 574
 Soybeans, 830
 Soy urease, 684
 Spark, aluminum, 38, 44
 as ultraviolet source, 38-45
 cadmium, 155
 carbon, 154
 cobalt, 44
 condensed, 42
 discharge, theory, 39-42
 gaps, 43, 44
 iron, 38, 152
 irradiated, 269
 lead, 155
 magnesium, 155
 molybdenum, 154
 nickel, 154
 reactions induced by, 45
 sources for photochemical reactions, 43-45
 spectra, 32, 33, 36, 42
 Tesla, 155
 tin, 155
 tungsten, 152, 154, 155
 uncondensed, 40
 underwater, 152, 153, 155
 uses, 38-45, 650
 zinc, 44, 154, 155
 Spawn, frog and toad, 766
 Specific heats and quantum theory, 17, 217
 Spectra, absorption, 152-163, 213, 214, 216, 218, 270, 271, 336, 337
 of sterols during irradiation, 794-801
 atomic, 19-22, 230
 band, 19, 163, 216-228
 continuous, 18, 19, 94, 152, 153, 229-236
 convergence, 230, 246, 293-295
 electron-affinity, 337, 338
 for absorption studies, 152
 line, 5, 18-23, 26
 molecular, 19, 217-228, 230, 231, 234-236
 of ions, 33
 of polyatomic molecules, 223, 224
 predissociation, 241-244
 Raman, 222, 224
 rotation-vibration, 221-223, 225
 series, 23, 24
 spark, 32, 33, 36, 42
 Spectrograph, 183, 190, 270, 271
 Spectrographic analysis, 662
 Spectrometer, quartz, 693, 694
 Spectrophotometers, photoelectric, 271
 Spectroradiometer, 100
 Spectroscopy, and photochemistry, 229-244, 270
 Spectrum, electromagnetic, nature, 2, 3, 6, 7, 9, 10
 of sunlamp, 144-146
 solar, 4, 7, 174, 192
 Spekker photometer, 161, 270
 Sperm, 717, 764
 Sperry arc, 618
 Spin, of electrons, 25, 226
 nuclear, 226
 Spinach, irradiated, 742, 789, 830, 856
 Spinal fluid, gold test, 677
 Spindle oil, 653
 Spirit black, 643
 Spirocyclopentane, 810
 Spirogyra, 685, 882
 Spirostomum ambiguum, microirradiation, 703
 Spleen, and typhoid immunization, 757
 Splenic hormone, 749, 750, 757
 Spores, 706, 711, 727
 Springfield Lake, solar energy at, 198-200
 Spruce, 618, 876
 Stryggyra, ultramicroscopic irradiation, 717
 Squalene, 511
 Square root law, for rates, 251, 252, 254, 278
 Stabilizers, 462, 657
 Stability of colloidal systems, 387, 388
 Stains, from methylene blue, 630, 631
 Standards, of radiation, 99, 100
 Stannates, and cotton, 615
 Stannic acids, 366, 591
 Stannic chloride, 489, 648
 hydroxide sol, 390, 391
 iodide, 240, 365, 366
 oxide, 259
 Stannous chloride, 365, 384
 oxide, 171
 Staphylococci, 706, 720, 727, 728, 825
 Staphylococcus aureus, 694, 696, 697, 704, 705
 phage, 712
 Star spectra, 32-34
 Starch, 267, 384, 435, 620, 681, 682, 791
 photolysis, 435, 436
 photosynthesis, 866-868, 882
 Starfish eggs, 764
 Stark effect, 163, 336
 Stearates, 586
 Stearic acid, 265, 266, 437, 554, 560, 574, 743
 anilide, 265, 677
 Stearolic acid, 565
 Steels, 661
 Steenbock diet, 786
 unit, 835, 838, 841
 Stefan-Boltzmann law, 15-17
 Stellar energy, origin, 191, 192
 Stenobothrus spermatoocytes, 704
 Stereoisomerizations, 406, 412, 452-456, 482-484, 488, 490, 491, 564-567, 569, 596, 793
 Stereoisomers, absorption by *cis* and *trans* forms, 453
 "Sterilamps," 724
 Sterilization, of food products, 721-724
 of medicinal products, 725-728
 of water, 125, 718-721
 Sterols, 789, 791-801, 809, 827, 833, 834, 888
 Stibine, 332
 Stigmasterol, 7-dehydro, 817
 Stilbazoles, polymerization, 521
 Stilbene, 267, 490, 511, 548, 549, 648, 743
 Stimulation of bacterial growth, 697
 of cells by ultraviolet rays, 697, 704, 707
 of paramecia, 717
 of plant growth, 150, 887
 of yeast growth, 708, 710
 Stinging nettles, 657
 Stokes's law, 207
 Stratification, of suspensions, 391
 Stratosphere, 193, 194
 Stratum granulosum, 736
 Straw pulp, 618
 Streaming reactions, temperature coefficients, 248
 Streptococci, 706, 727
 Striated discharge, mercury vapor, 83
 Strontium, 26, 57, 184
 Strophanthus, tincture, 658
 Strychnine, 525
 Styene, 173, 488, 489, 595
 Styrolene, 548
 1-Styryl-3-bromostyryl-4,6-dinitrobenzene, 471
 4-Styryl-2,4-dichloro-3-cyanopyridine, 521
 Substance 248 in ergosterol irradiation, 808, 811, 821
 Substance I, in ergosterol irradiation, 805, 807
 Substance S in ergosterol irradiation, 800, 801
 Succinic acid, 437, 438, 441, 447, 452, 454, 764
 Succino-dehydrogenase, 686, 687
 Sucrose, 682, 683
 Sucrose, 260, 356, 371, 387, 433-435, 472, 521, 868, 890
 Sugars, 500, 681, 682, 722
 occurrence, 742, 858, 891
 oxidation, 673
 photosynthesis, 866, 870, 889 (see also Carbohydrate photosynthesis)
 Sulfanilic acid, 500, 643
 Sulfate ion, 355, 377
 Sulfhydryl compounds, 463, 623, 676, 678, 679
 Sulfides, 142, 583, 615
 Sulfite cellulose, fluorescence, 620
 Sulfites, 355, 356

- Sulfobenzeneazo-*N*-phenyl- β -naphthylamine, 626
 Sulfonfluorene, 503
 Sulfones, 489
 Sulfonic acids, 519
 Sulfophenyl-3-methyl-5-pyrazolone, 382
 Sulfur, 141, 359, 390, 534, 600, 605, 607, 611, 620
 and gasoline, 654
 and oils, 558, 574
 bacteria, 518
 compounds, 379, 463, 464, 534, 653-655
 fluorescence, 600, 601, 620
 formation, 354, 358, 385, 463, 498
 in vulcanization, 597-599
 neutral, excretion, 745
 occurrence, 608, 622, 623, 679, 756
 oxidation, 354
 pigment, 582
 predissociation, 241, 244
 reaction with arsenic, 354
 reaction with hydrogen, 329
 sensitizer, 479
 sols, 387, 390
 vapor, absorption spectrum, 329
 Sulfur chlorides, 354, 355, 534, 545, 596, 599
 dioxide, 69, 330, 332, 390, 407, 534, 590, 634, 654, 750
 absorption spectrum, 330, 355
 from wool, 622
 in accelerated paint tests, 580
 predissociation, 241, 243, 244, 330
 monoxide, 330
 oxygen acids, formation, 354
 trioxide, 330
 Sulfuric acid, 187, 339, 343, 354, 469, 484
 effect on various photoreactions, 340, 358, 455, 524
 formation, 331, 357, 457
 Sulfurous acid, 354
 Sulfuryl bromide, 332
 Sulfuryl chloride, 331, 534, 545
 Sulzin, 598
 Sun, as ultraviolet source, 99, 191-202
 "Sun Ray," 173
 Sunburn, 673, 733
 creams, 743
 Sunflower, 886, 888
 oil, 571, 574, 790
 Sunlamp, 111, 141, 143-147, 561, 738, 783, 887
 Alpine, 129, 134, 135
 Sunlight, actinometry of, 35, 103-105
 and rickets, 170, 778, 779, 781, 782, 787, 809, 828, 832, 837
 antagonistic action of rays in, 150
 energy distribution, 192, 195-202
 tests of light-fastness of dyes, 634-636, 640-642
 therapeutic use, 734, 769, 770, 772, 773
 "Sunlit," 175
 Sunspots, 2, 192
 Suprasterols, 805, 808-811
 Surface catalysts, 253, 254
 designs, on rubber, 599
 photoreactions in, 265
 vulcanization, 598, 599
 Swan hands, in carbon arc, 53
 Swatch boxes, 640
 Swimming pools, 147, 720
 Swine, light sensitization, 861
 "Sylphrap R R Old Gold," 561
 Sympathetic system, 734, 760
 Sympathicotonic action, 751
 Symplex, of vitamin D and lactalbumin, 839
 Sympnehrine, 689
 Synergy, of radiations, 442, 443, 486, 873
 Synthetic rubber, 409, 593
 Tar cancers, 766
 coal, 865
 papillomas, 766
 road, testing, 661
 Tarric acid, 554
 Tartar emetic, 359
 Tartaric acid, 384, 407, 448, 450, 541, 648, 660, 672, 870, 883
 oxidation, 364, 366, 448, 450
 Tartrates, 353, 377
 Tea, 660
 Teaseed oil, 555
 Teeth, 178, 824
 Television, 150
 Telfairia oil, 574
 Tellurium, 148, 384
 oxide, 354
 Temperature, after body irradiation, 744
 and absorption spectra of solutions, 337
 and black body radiation, 15-17
 and photosynthesis in plants, 873, 874, 876, 882
 effect on lamps, 132, 133, 139
 coefficient, 245, 248-250, 252, 293, 443, 692, 693, 698, 708, 711, 716, 740
 Tenderizing beef, 724
 Tent fabrics, 615
 Terephthaldehyde, 476, 481, 482
 Terephthaldehydic acid, 476, 481
 Terephthalic acid, 481
 Terephthalophenone, 476
 Terms, spectral, 23, 24, 234, 235
 Terpenes, 514, 550, 659
 Terpinol hydrate, 514
 Tesla coil, 153
 spark, 155
 Test, accelerated weathering, asphalts, 661
 dyes, 634-642
 enamels and lacquers, 586, 587, 590
 lithopone, 386
 paints, 575-581
 papers, 618
 road tar, 661
 rubber, 605-609
 steels, 661
 varnishes, 586, 587
 Tetanus bacillus, 710
 toxin, 690
 Tetany, 755, 823, 826
 Tetrabenzoylthylene, 489, 490, 493
 Tetraborate ion, 377
 Tetrafluoromethylfluorescein, sensitizer for Eder reaction, 444
 Tetracarboxypyridine, 519
 Tetrachloroanthraquinone, 550
 Tetrachloroarsine, 549
 Tetrachlorobenzene, 547
 Tetrachlorodimethylbenzophenone, 478
 Tetrachlorodimethylbenzoyl chloride, 548
 Tetrachlorodithiacyclobutane, 464
 Tetrachloroethane, 401, 526, 537, 613
 Tetrachloroethylene, 534, 535, 657, 659
 Tetrachloroketomaphthalene, 493
 Tetrachloromethylpropane, 532
 Tetrachloroplatinic acid, 248, 369, 370
 Tetraconite, 613
 Tetrafluorenylhydrazine, 511
 Tetrahydrodiphenylinaphthacene, 510
 Tetrahydronaphthalene, 613
 Tetraleneacetic acid, 511
 Tetralin, 501, 657
 Tetramethoxyaminophenylcinnamic acid, 484
 Tetramethoxyphenylcarbostyryl, 484
 Tetramethylene, nitroschloride, 461
 Tetramethylthiuramdisulfide, 598, 605, 612
 Tetranitrodiammine cobalt, 368
 Tetranitromethane, 36
 Tetraoxybutyloxquinioxaline, 851
 Tetraoxybutylquinioxaline, 851
 Tetraphenylidibenzoyltetrahydropyran, 521
 Tetraphenylidihydropyridine, 521
 Tetraphenylidihydrotriazine, 493
 Tetraphenylidihydroxyethanedicarboxylic acid, lactone, 478
 Tetraphenylrubene, 509
 Tetraphenylrubrene, 510

- Textile printing, 520, 645-647
 Textiles, 4-9, 624, 641, 831
 Thallium, 150, 238, 257, 369, 377, 380, 744
 bromide, 238
 chloride, 183, 238, 350
 iodide, 238, 345
 Theosterols, 817
 Therapy, 143, 150, 770-772, 862
 lamp, 132-134, 138, 139
 Thermionic valve, 97
 Thermochemistry, 217
 Thermocouple, 771
 Thermodynamics, and photochemistry, 206, 212, 213
 Thermoluminescence, of solarized glasses, 176
 Thermophilic bacteria, 722
 Thermopiles, 96, 99, 271, 697, 782
 Thermostat, for carbon arc, 60
 Thiamine, 850, 851
 Thiazine dyes, 640, 712
 Thiazole, amino, 498
 Thiazoline, 183
 Thiocarbamide, 498
 Thiocarbamide, 573, 605
 Thiochrome, 851
 Thiocresol, 415
 Thiocyanic acid, 358
 Thiocyanacetoneoxime, 494
 Thiocyanogen, 457
Thiocystis, 707
 Thioglycolic acid, 463
 Thiohydrazides, condensation products of, 500
 Thionine, 631
 Thiophene, 466, 863
 Thiophosgene, 463, 464
 Thiopyronine, 712
 Thiosemicarbazones, 495
 Thiosinamine, 263, 264, 864
 Thioxanthone dyes, 712
 "Thiozone," 597
 Thistle blossom rennet, 684
 Thoracoplasties, 729
 Thorium, 97, 98, 362
 dioxide, 870
 hydroxide sol, 390, 391
 Thormahlen reaction, 740
 Threads, sterilization, 727
 Thresholds, for lethal action, 699-701, 716
 for vitamin D₂ formation, 812
 photochemical, 246, 247, 290, 291, 327, 397, 480, 866
 photosynthesis of carbohydrates, 866
 Thrombin, 684
 Thrombocytes, 749, 825
 Thrombocytopoiesis, 749
 Thrombopenia, 749
 Thunberg tube, 686
 Thyme oil, 513
 Thymine, 518, 696, 699, 701, 702
 glycol, 518
 Thymol, 513
 Thymonucleic acid, 677, 698-701, 704
 Thyroid gland, 689, 749, 759, 777
 "Timonox," 582
 Tin, 149, 150, 155, 171, 365, 366, 386, 657
 halides, 359, 411
 Tinctures, deterioration, 658
 Tires, fluorescence analysis, 600
 Tissue cultures, 764, 765
 paper, 619, 620
 respiration, 863
 Titanium, 26, 57-59, 78, 97-99, 172, 592, 743
 chlorides, 359, 369
 dioxide, 165-169, 458, 609, 612, 617, 673, 883
 nitride, 139
 oxide, 75, 152, 350, 386, 583, 598
 white, 575, 582, 590
 "Titanox," 577, 582, 583
 "Tithonometer," 284
 Titrations, in Wood's light, 665
 Tobacco, 522, 659, 660, 861
 cloth, 616
 disease virus, 712
 plants, 883, 884, 889
 Töpler cloud, 285
 Tolidine, 646, 721
 Tolualdehydes, 469
 Toluene, 467-469, 470, 480, 496, 506, 508, 514, 651
 acetyl, 547
 arsenic acid, 549
 Tolueneazo- β -naphthol, 633, 634
 bromination, 545, 549
 chlorination, 526, 542, 544, 545
 chloro, 544, 549
 hexahydro, 424, 473
 nitro, 470-472
 sulfonanilide, 587
 Toluidine, 474
 Toluic aldehyde, 468
 Toluidine Blue, 632
 Green, 632
 Toluidines, 495, 497, 647
 Toluquinone, 474
 Tollybenzoic acid, 478
 1,1'-bis-(*p*-Tolyl)-3,3'-diphenyl-5,5'-dimethylrubrene, 510
 Tolyglyoxime, 461
 Tolyquinoline, 521
 Tomato bushy stunt virus, 712
 plants, 887-889
 "Toplast," 589
 Torch, oxyacetylene, 164
 Tortelli-Jaffe reaction, 796
 Tortoise shell, bleaching, 649
Torula, 685
Toxascaris Leonina, ova, 718
 Toxic calcification factor, 821
 Toxicity, mercury, 124
 vitamin D, 820-823
 Toxins, 690, 691, 860
 Toxisterol, 808, 811, 821
Toxocara ova, 718
 Tracing cloth, 189
 Transformer oils, 651
 Transformers, 40, 42, 135, 136, 139, 140, 144, 147, 153-155, 159, 162
 Transitions, between energy states, 219-223, 225
 forbidden, 24, 92
 Transpiration, 867, 874
 Trehalose, hydrolysis, 434
 Triacetin, 650
 Triacetoxvtriethanolamine, in stabilizing gasolines, 655
 Triaminotriphenylmethane, 626
 Triarylacetoneitriles, 627
 Triazine tetraphenylidihydro, 493
 Triazolium salts, 626
 Tribromoethyl alcohol, 658
Tribulus terrestris, as photosensitizer, 861
 Tributyl phthalate, 576
 Trichloroacetic acid, 249, 452
 Trichloroacetyl chloride, 534, 535
 Trichloroacetyltrichloromethylbenzene, 547
 Trichlorobenzene, 543, 547
 Trichlorobromomethane, 211, 215
 Trichloroacetic acid, 550
 Trichloro-2,4-dimethylbenzoyl chloride, 548
 Trichloroethane, 534
 Trichloroethylene, 401, 407, 529, 535, 657
 Trichlorohydrin, 534
 Trichloroiodobenzene, 544
 Trichloroisobutane, 532
 Trichloromethylpropane, 532
 Trichloropropane, 534
 Tricresyl phosphate, 576, 590, 591
 Triethanolamine, 833
Trifolium, 715
 Trihexosan, 435
 Trihydroxyanthraquinone Purpurin, 616
 Trihydroxytriethylamine derivatives, 183
 Tri-iodide ion, 249, 446
 Trimethylacetaldehyde, 421
 Trimethylamine, and visual purple, 858
 Trimethylenechlorohromide, 550
 Trimethylethylene, 394, 594
 Trimethylindostannane, 366
 Trimethylisalloxazine, 852
 Trimethylmethane derivatives, 267
 Trimethylpentane, 464

- Trinitrobenzaldehyde, 475
 Trinitrobenzene, and rubber vulcanization, 598
 Trinitrobenzoic acids, 472
 Trinitrobenzoyl alcohol, 472
 Trinitrobenzyl bromide, 472
 Trinitrostilbene, 266, 267
 Trinitrotoluene, 354, 471, 472
 Trinitrotriamine cobalt, 368
 Triolein, 558
 Triose, 435, 436
 Triphenylbromomethane, 626
 Triphenylchloromethane, 626, 627
 Triphenylfulgide, 493
 Triphenylguanidine, 605, 610
 Triphenylhydroxypropionic acid, 477, 478
 Triphenyllactic acid, 477, 478
 Triphenylmethane and derivatives, 267, 626-629, 632, 640
 Triphenylnaphthacene, 511
 Triphenyl peroxide, 626
 Triphenyl phosphate, 173, 590
 Triphenylrubrene, 510, 511
 Trisilane, 333
 Trisodium phosphate, 440
 Trisulfon Violet, 639
 Tritolyl phosphate, 587, 589, 591
 Triton embryos, 765
 Tropacocaine, 436
Tropaeolum majus, photosynthesis, 868
 "Tru-hu" silk crepe, 642
 Truxilidamide, 484
 Truxillic acid, 483, 484, 491
 Truxinic acid, 483, 491
 Truxinic anhydride, 484
 Truxones, 492, 493, 517
 Trypanflavine, 261, 264, 861, 862
 Trypan Blue, 634
 Red, 634
 Trypsin, 680, 684
 Tryptophane, 670-674, 682, 683, 696, 701, 737, 739, 748, 764, 863
 Tsubaki oil, oxidation, 559
 Tubercle bacilli, 699, 706, 775
 Tuberculin, 690
 Tuberculinic acid, 700
 Tuberculosis, 733, 771-773, 823
 Tumors, 150, 742, 766, 865
 Tuna fish liver oil, 801, 815-817
 Tung oil, 386, 559, 564-567, 571, 648
 Tungstates, and cotton, 615
 Tungsten, 58, 59, 74, 75, 78-80, 143, 145, 149, 156, 161, 369
 lamp, 34, 35, 156, 160, 693, 694
 spark, 152, 154, 155
 Tungsten carbide, 51
 trioxide, 369
 Tungstic acid, 369, 387, 418, 433
 Turkey-red oil, 382, 613
 Turnip seeds, 716, 885
 Turpentine, 513, 514, 610
 Tyndall cone, 387
 Typhoid bacillus, 720, 757, 775, 825
 Tyrosinase, 684
 Tyrosine, 670-674, 682, 684, 696, 701, 737, 739, 741, 791, 863

U
 hands, in halide crystals, 375
 Ulcers, 862
 Ultrament, 562
 Ultramicroscopic irradiation of protozoa, 717
 Ultramicroscopy, of dried oils, 567
 "Ultratuberculin," 690
 "Ultraviol," 175
 Ultraviolet microscopy, 703, 704, 715
 Ultraviolet-permeable glasses, 168-176
 Ultraviolet plates, 381, 382
 radiations, 2, 6, 7, 164, 208, 498
 Ultraviolet-sensitive papers, 383
 Ultraviolet-transmitting materials, 172-176
 "Ultrazin," 166
Urea lactuca, photosynthesis by, 874
 Umbelliferoneacetic acid, 562
 Undecenic acid, 553
 Units, for milk irradiation, 842, 843, 845, 846

 Units, photosynthetic, 881
 vitamin D, 781, 819, 820
 wave-length, 5
 Unsaturated acids, bromination, 554
 compounds, aliphatic, 406-415
 hydrocarbons, halogenation, 533-538
 oils, detection, 558
 Uracil, 677, 683, 696, 699, 701-703, 850
 Uranic salts, 361
 Uranin, 261
 Uranium, 58, 97-99, 103-105, 155, 169, 370
 acetate, 834
 ferrocyanide sol, 391
 nitrate, 178
 oxides, 166, 630, 868
 salts, 359, 362, 370, 403, 407, 432, 450, 468, 727
 Uranous sulfate, 370
 Uranyl acetate, 448, 525
 chloride, 489
 nitrate, 405, 411, 442, 449, 481, 503, 812
 oxalate, 102, 104, 418, 443, 459
 salts, 259, 261, 336, 409, 439, 440, 443, 447, 451, 452
 sulfate, 104, 307, 447
 Urea, 171, 173, 356, 436, 498, 688, 760
 condensation with formaldehyde, 172, 584
 derivative of aminobenzoylphenylenediamine, 562
 diethyldiphenyl, 354
 formation, 350, 518, 702
 of 4-aminobenzoyl-3-aminopyrenedisulfonate, 562, 563
 photolysis, 458, 459
 Urease, 683, 684
 Urethane, and quinine, 523
 Uric acid, 187, 350, 702, 703, 863
 Urine volume, 745
 Urobilin, 750
 Urobilinogen, 871
 Uroflavin, 851
 Uronic acid, 883
 "Uroxameter," 103
 "Ursilber," 379
 Urticaria, 824, 861, 862
 Uterus, 760
 "Uviarc," 80, 81, 85-87, 89, 92, 100, 117, 129, 134-137, 174, 175
 "Uviol," 156, 173, 175, 176, 178, 182, 305
 lamps, 108, 114, 182
 "UVscope," 100

V
 accination, 713, 775
 Vaccines, bacterial, 725, 726
 Vaccinia virus, 712, 725
 Vagotonic action, 751
 Vagus, 734, 746
 Valve, 671
 Valve, thermionic, 97
 Vanadium, 26, 58, 169
 oxide, 75, 152, 165-167, 508
 salts, 409, 592
 Vanillin, 498, 514, 558
 Van Slyke test for amino groups, 622
 Varnishes, 407, 566, 573, 586, 587, 648
 Vaseline, 381, 462, 600, 610, 727
 Vasoconstriction, 747
 Vasodilatation, 747
 Vials, 616, 617, 630, 642, 647
 Vegetable extracts, 722
 oils, 557, 789
 Vegetables, vitamin D in, 827
 Venom, cobra, 691
 Vermillion, 386
 Veterinary medicine, irradiation therapy in, 777, 785, 786
 "Viat," 173
 Vibrational energy, 218, 220, 222, 223, 227, 229, 230, 233-236, 247, 250
 Vibrationless state, 233
Vicia faba, leaves, 715
 Victor water-cooled mercury arc, 701
 Victoria dyes, 636, 639, 554
 Vgantol, 759, 820, 821, 825, 832, 833
 Villikin, 689
 Vinyl acetate, 172, 173, 410, 411, 585
 anisole, 410

- Vinyl bromide, 409, 410
 chloride, 409-411, 534, 585
 chloroacetate, 173
 diazomethane, 460
 esters, polymerization, 173, 410, 411
 ethynylcarbinols, 410, 411
 halides, 205, 410, 411
 iodide, 399
 resin, 410-412, 619
 Violet N, 639
 Violin strings, sterilization, 727
 "Viopake," 166
 Viosterol, 742, 820, 823-827, 831
Vipera Russellii, toxin, 691
 Viruses, 711-713, 860
 Viscose, 188, 585, 613, 615, 616, 619-621
 Viscosity, and fluorescence quenching, 335
 Visibility, sensitivity curve, 180
 short wave-length limit, 762
 Visible rays, 2-4, 6, 178, 208, 680, 692
 Vision, 856-859
 Visual yellow, 858
 purple, 857-859
 "Vitaglass," 103, 104, 169, 172-175, 178, 181, 637, 661, 711, 712, 776, 782, 825, 887, 888
 Vital staining, 751
 "Vitamalt," 832
 Vitamin, antihemorrhagic, 856
 fat-soluble, 780
 preparations, standardization, 834
 production, 848
 Vitamin A, 814, 825, 828, 846, 848, 857, 858
 absorption spectrum, 853
 assay, 780, 853, 854, 856
 in cod-liver oil, 831
 not produced by irradiation, 780, 790
 photolysis, 854-856
 Vitamin A₂, 853
 Vitamin B group, 688, 850-853
 Vitamin C, 660, 740, 743, 755, 785, 846, 848, 849
 Vitamin D, absorption spectrum, 796-799, 804
 and infections, 823-825
 and public health, 831
 assay, 780, 785, 805
 crystalline, 800, 801, 803-807
 destruction, 721, 793, 797, 801, 803, 805
 dosage, 802, 803, 819, 820
 emulsion, 834
 for animals, 786, 788, 838
 formation, 103, 150, 733, 803, 804, 814, 832
 in human milk, 785
 in wine, 660
 local application, 847
 natural, 813, 814, 816
 origin in fish-livers, 790
 physiological action, 780, 785, 818, 819, 824, 827
 response of rats and chicks, 814, 817
 toxicity, 785, 820-823
 unit, 781, 819, 820, 835
 Vitamin D₁, 806, 807, 821
 Vitamin D₂, 803, 807, 808-811, 813-817, 821, 822, 834
 Vitamin D₃, 816, 817, 821, 831
 Vitamin D₄, 813
 Vitamin E, 856
 Vitreous humor, transparency, 762, 764
 "Vitrisol," 742
Voandzeia, 715
 Voltaic cells, irradiation of, 105
Vorticella, 523
 Vulcanization, 596-599, 601, 604, 605
 Vulcanized rubber, 593, 597, 601, 606-608, 609
 Vulkan colors, 599
 Vuzin, 524
 Warburg respiratory enzyme, 687
 Washington, solar energy at, 195, 198
 Water, 359
 absorption, 183, 194, 298, 299, 338
 bands, fluorescence, 304
 dissociation, 231, 240, 299, 302
 effect of x-rays on, 209
 effect on carbon dioxide photolysis, 307, 308
 effect on hydrogen-chlorine combination, 286-288
 filters, 183
 formation, 299, 302-304, 422
 irradiated, 710, 720
 photolysis, 299, 339
 reaction with bromine, 345
 sterilization, 718-721
 Water gas, 259, 481
 Water-glass, 385
 Waterproofing paper, 620
 Wave-length, and temperature coefficients, 249, 250
 characterizing radiations, 10, 11
 conversion to wave-number, 208
 optimum for lethal action, 698, 701
 effective for milk irradiation, 843, 844
 effective in rickets, 780, 781, 809
 effective in therapy, 773
 erythema-producing, 737, 738
 for lethal action on yeast, 708
 kcal, equivalent of, 207, 208
 measurement, 4, 5
 restricted, in irradiation of ergosterol, 833, 834
 synergy of, 450
 Wave mechanics (see Quantum mechanics)
 Wave-number, 5, 208, 222, 224
 Wave theory, 3, 4, 6, 10
 Waxes, 2, 3, 4, 6
 Wax, carnauba, 608
 ceresin, 610
 Japan, 586
 Montan, in rubber, 610
 white, 534
 Waxes, fluorescence, 600
 Weather-Ometer, 587
 Wedges, platinum for reducing light intensity, 270
 Wehnelt cathodes, 76, 156
 Weigert effect, 266, 383
 Welding, injury to eyes, 164
 Weston photonic cell, 97
 Whale oil, 555, 557
 Wheat, 829, 830, 883
 Whitby test for cholesterol, 793
 White cells (see Leucocytes)
 White lead, 582, 583
 Whitong, in rubber, 610
 Whiskey, aging, 660
 Whooping cough, 775
 Wien's displacement law, 15, 16, 94, 155
 Willemite, 190
 Window glass, 170, 174, 175
 Wine, aging, 660
 Wintergreen oil, 513
 Winter sunlight, and rickets, 781, 782
 Witte's peptone, 674, 688, 691
 Wood, 611, 612, 617-619, 648
 Wood's light, 461, 752, 781, 849
 Wool, 188, 189, 613, 616, 618, 622, 623, 678, 679
 and dyes, 471, 635, 637, 639, 501, 502
 chlorination, 550
 fat, irradiated, 847
 fluorescence, 624, 645
 Green, 642
 mold growth on, 727
 Woolen patterns, 642, 643
 Wormseed oil, 513
 Worsted, 636, 640, 642
 Wort, irradiation, 710
 Wound healing, 729, 770
 Wrappers, protective, 560-563
 Wurtzite, 385
 Xanthene dyes, 640
 Xanthine, 702
 Xanthine oxidase, 686
 Xanthogenation, 617
 Xanthone, 507
 Xanthophyll, 856, 858, 871, 872, 876, 882, 888
 Xanthorhammin, 436
 Xanthrydrol, 592
 Xenon lamp, 151, 300, 308, 319, 393
 Xeroderma pigmentosum, 769, 861
 Xerophthalmia, 780
 X-rays, 2, 7-9, 354, 657
 and foodstuffs, 828
 and proteins, 677
 and sterols, 803, 804, 832

X-rays, biological actions of, 705, 708, 733
reactions by, 208, 209
Xylene, 467-469, 503, 545, 546, 651, 829
Xylidine, 497, 647
Xylyl chloride, 546

Y
Yarns, 613, 615
Yeast, absorption spectrum, 708
and glucolysis, 710
antirachitic activation of, 837
autolyzates, 682, 683, 837, 847
catalase content, 685
destruction of B vitamins in, 850
effects of irradiation of, 707-710, 727, 789
ergosterol content, 795
extract, 686, 837
growth, 563, 708, 709
gums, 682
proteinase, 683
respiration, 687, 688, 709, 750
susceptibility to lethal action of rays, 696, 706
Yellow oxidation enzyme, 853
Yttrium compounds, 58, 142

Z
Zapon lacquer, sensitizer, 479
Zea mays, seedlings, 888
Zeeman effect, 24
Zero branch, 223
Zero-point energy, 227, 233, 235, 290
Ziehl-Neelsen stain, 706
Zinc, 97, 147, 150, 151, 169, 171, 190, 385, 541
and fatty acids, 554
arc, 62, 64, 231
corrosion, 661
glass, 165
heat of dissociation, 234
in carbon arc, 57
in tissues, 760
lamp, 148-150

Zinc, plates, and aniline, 495
soaps, 586
sols, 387, 388
spark, 154, 155
wool, 401
Zinc blende, 385
carbonate, 869
chloride, 64, 171, 519, 532
chromate, 583
diethyl, 464
diethyldithiocarbamate, 605
dimethyl, 464
disulfide, 385
halides, 240, 411
nitride, 64
oxide, 169, 171, 178, 575, 590, 605, 831
and dyes, 630
and nitrate reduction, 354
as photosensitizer, 259, 339, 350, 370, 371,
458, 500, 553, 625, 673, 883
fluorescence analysis, 600, 601
in carbohydrate photosynthesis, 869
in nitrocellulose lacquers, 580, 589
in rubber, 598, 599, 603, 607, 610, 611
opacity, 582
paints, 577, 580
reflecting power, 583
oxynitrate, 371
peroxide, 573
resinates, 585
salicylate, 621
silicate, 142
sulfide, 384, 385, 590, 600, 743
actinometer, 104, 105, 202, 717
xanthate, 596
Zirconium, 58, 59, 362
nitride, 139
oxide, 141
Zones, in crystals, 374, 375
Zoöplankton, 790
Zwitterions, 671
Zygote, 717
Zymosterol, 795



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